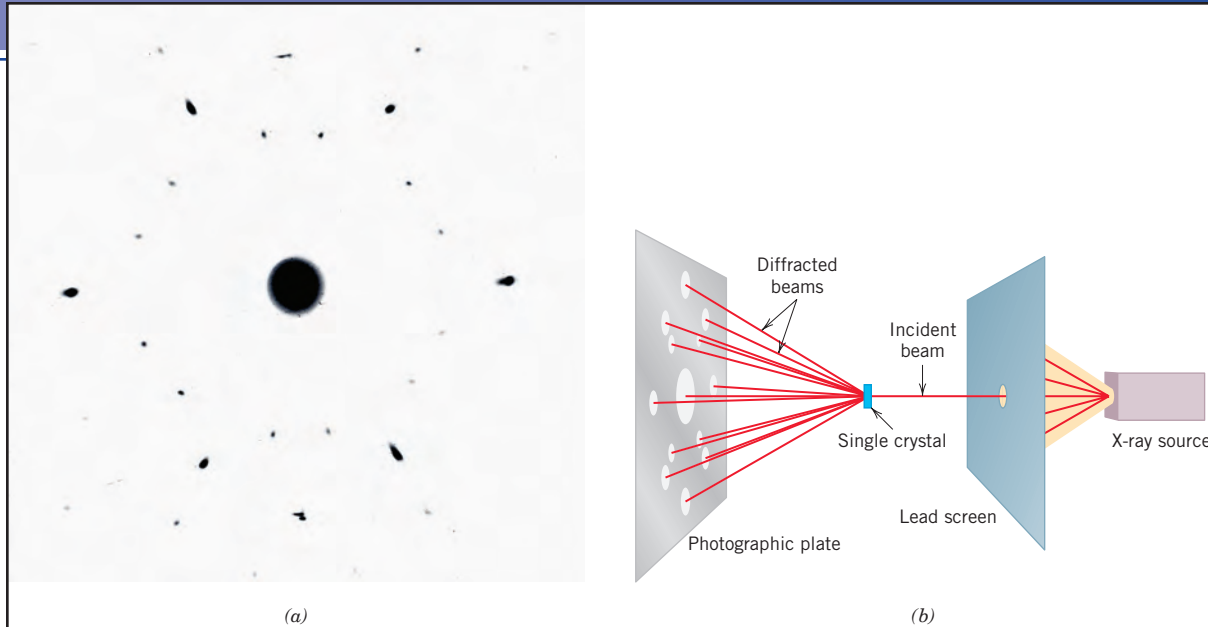


Chapter 3 The Structure of Crystalline Solids



(a) X-ray diffraction photograph [or Laue photograph (Section 3.16)] for a single crystal of magnesium. (b) Schematic diagram illustrating how the spots (i.e., the diffraction pattern) in (a) are produced. The lead screen blocks out all beams generated from the x-ray source, except for a narrow beam traveling in a single direction. This incident beam is diffracted by individual crystallographic planes in the single crystal (having different orientations), which gives rise to the various diffracted beams that impinge on the photographic plate. Intersections of these beams with the plate appear as spots when the film is developed.

The large spot in the center of (a) is from the incident beam, which is parallel to a $[0001]$ crystallographic direction. It should be noted that the hexagonal symmetry of magnesium's hexagonal close-packed crystal structure is indicated by the diffraction spot pattern that was generated.

[Figure (a) courtesy of J. G. Byrne, Department of Metallurgical Engineering, University of Utah. Figure (b) from J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Copyright © 2004 by John Wiley & Sons, Hoboken, NJ. Reprinted by permission of John Wiley & Sons, Inc.]

WHY STUDY *The Structure of Crystalline Solids*?

The properties of some materials are directly related to their crystal structures. For example, pure and undeformed magnesium and beryllium, having one crystal structure, are much more brittle (i.e., fracture at lower degrees of deformation) than are pure and undeformed metals such as gold and silver that have yet another crystal structure (see Section 7.4).

Furthermore, significant property differences exist between crystalline and noncrystalline materials having the same composition. For example, noncrystalline ceramics and polymers normally are optically transparent; the same materials in crystalline (or semi-crystalline) form tend to be opaque or, at best, translucent.

Learning Objectives

After studying this chapter you should be able to do the following:

1. Describe the difference in atomic/molecular structure between crystalline and noncrystalline materials.
2. Draw unit cells for face-centered cubic, body-centered cubic, and hexagonal close-packed crystal structures.
3. Derive the relationships between unit cell edge length and atomic radius for face-centered cubic and body-centered cubic crystal structures.
4. Compute the densities for metals having face-centered cubic and body-centered cubic crystal structures given their unit cell dimensions.
5. Given three direction index integers, sketch the direction corresponding to these indices within a unit cell.
6. Specify the Miller indices for a plane that has been drawn within a unit cell.
7. Describe how face-centered cubic and hexagonal close-packed crystal structures may be generated by the stacking of close-packed planes of atoms.
8. Distinguish between single crystals and polycrystalline materials.
9. Define *isotropy* and *anisotropy* with respect to material properties.

3.1 INTRODUCTION

Chapter 2 was concerned primarily with the various types of atomic bonding, which are determined by the electron structures of the individual atoms. The present discussion is devoted to the next level of the structure of materials, specifically, to some of the arrangements that may be assumed by atoms in the solid state. Within this framework, concepts of crystallinity and noncrystallinity are introduced. For crystalline solids the notion of crystal structure is presented, specified in terms of a unit cell. The three common crystal structures found in metals are then detailed, along with the scheme by which crystallographic points, directions, and planes are expressed. Single crystals, polycrystalline, and noncrystalline materials are considered. The final section of this chapter briefly describes how crystal structures are determined experimentally using x-ray diffraction techniques.

Crystal Structures

3.2 FUNDAMENTAL CONCEPTS

crystalline

Solid materials may be classified according to the regularity with which atoms or ions are arranged with respect to one another. A **crystalline** material is one in which the atoms are situated in a repeating or periodic array over large atomic distances; that is, long-range order exists, such that upon solidification, the atoms will position themselves in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest-neighbor atoms. All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions. For those that do not crystallize, this long-range atomic order is absent; these *noncrystalline* or *amorphous* materials are discussed briefly at the end of this chapter.

crystal structure

Some of the properties of crystalline solids depend on the **crystal structure** of the material, the manner in which atoms, ions, or molecules are spatially arranged. There is an extremely large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals to exceedingly complex ones, as displayed by some of the ceramic and polymeric materials. The present discussion deals with several common metallic crystal structures. Chapters 12 and 14 are devoted to crystal structures for ceramics and polymers, respectively.

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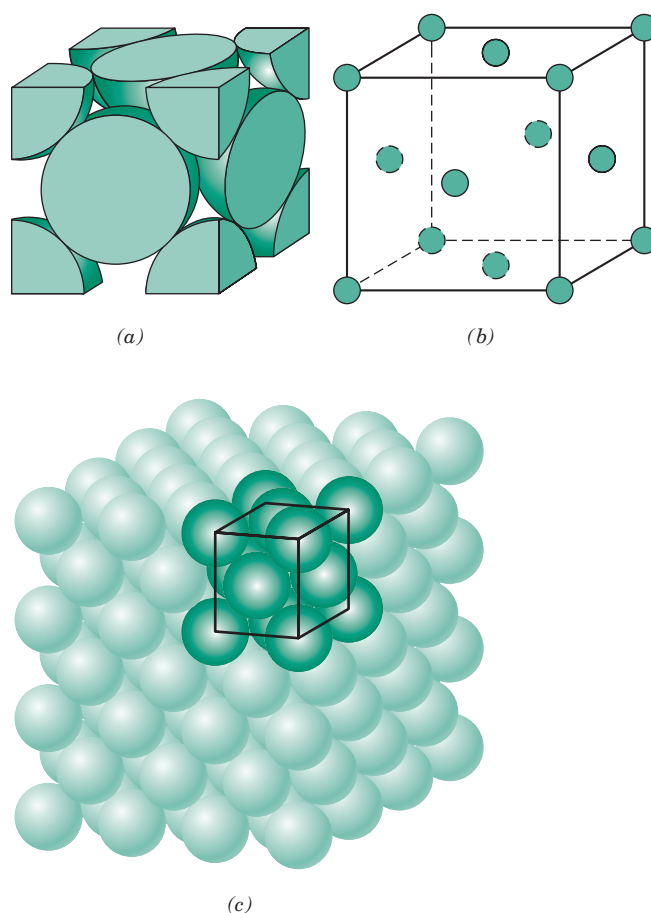


Figure 3.1 For the face-centered cubic crystal structure, (a) a hard sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms. [Figure (c) adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

When describing crystalline structures, atoms (or ions) are thought of as being solid spheres having well-defined diameters. This is termed the *atomic hard sphere model* in which spheres representing nearest-neighbor atoms touch one another. An example of the hard sphere model for the atomic arrangement found in some of the common elemental metals is displayed in Figure 3.1c. In this particular case all the atoms are identical. Sometimes the term **lattice** is used in the context of crystal structures; in this sense “lattice” means a three-dimensional array of points coinciding with atom positions (or sphere centers).

lattice

3.3 UNIT CELLS

unit cell

The atomic order in crystalline solids indicates that small groups of atoms form a repetitive pattern. Thus, in describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called **unit cells**. Unit cells for most crystal structures are parallelepipeds or prisms having three sets of parallel faces; one is drawn within the aggregate of spheres (Figure 3.1c), which in this case happens to be a cube. A unit cell is chosen to represent the symmetry of the crystal structure, wherein all the atom positions in the crystal may be generated by translations of the unit cell integral distances along each of its edges. Thus, the unit cell is the basic structural unit or building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within.

3.4 Metallic Crystal Structures • 41

Convenience usually dictates that parallelepiped corners coincide with centers of the hard sphere atoms. Furthermore, more than a single unit cell may be chosen for a particular crystal structure; however, we generally use the unit cell having the highest level of geometrical symmetry.

3.4 METALLIC CRYSTAL STRUCTURES

The atomic bonding in this group of materials is metallic and thus nondirectional in nature. Consequently, there are minimal restrictions as to the number and position of nearest-neighbor atoms; this leads to relatively large numbers of nearest neighbors and dense atomic packings for most metallic crystal structures. Also, for metals, using the hard sphere model for the crystal structure, each sphere represents an ion core. Table 3.1 presents the atomic radii for a number of metals. Three relatively simple crystal structures are found for most of the common metals: face-centered cubic, body-centered cubic, and hexagonal close-packed.

The Face-Centered Cubic Crystal Structure

The crystal structure found for many metals has a unit cell of cubic geometry, with atoms located at each of the corners and the centers of all the cube faces. It is aptly called the **face-centered cubic (FCC)** crystal structure. Some of the familiar metals having this crystal structure are copper, aluminum, silver, and gold (see also Table 3.1). Figure 3.1*a* shows a hard sphere model for the FCC unit cell, whereas in Figure 3.1*b* the atom centers are represented by small circles to provide a better perspective of atom positions. The aggregate of atoms in Figure 3.1*c* represents a section of crystal consisting of many FCC unit cells. These spheres or ion cores touch one another across a face diagonal; the cube edge length a and the atomic radius R are related through

$$a = 2R\sqrt{2} \quad (3.1)$$

This result is obtained in Example Problem 3.1.

For the FCC crystal structure, each corner atom is shared among eight unit cells, whereas a face-centered atom belongs to only two. Therefore, one-eighth of each of the eight corner atoms and one-half of each of the six face atoms, or a total of four whole atoms, may be assigned to a given unit cell. This is depicted in Figure 3.1*a*, where only sphere portions are represented within the confines of the cube. The

face-centered cubic
(FCC)

Unit cell edge length
for face-centered
cubic



Crystal Systems and
Unit Cells for Metals

Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

<i>Metal</i>	<i>Crystal Structure^a</i>	<i>Atomic Radius^b (nm)</i>	<i>Metal</i>	<i>Crystal Structure</i>	<i>Atomic Radius (nm)</i>
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

^a FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.

^b A nanometer (nm) equals 10^{-9} m; to convert from nanometers to angstrom units (\AA), multiply the nanometer value by 10.

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cell comprises the volume of the cube, which is generated from the centers of the corner atoms as shown in the figure.

Corner and face positions are really equivalent; that is, translation of the cube corner from an original corner atom to the center of a face atom will not alter the cell structure.

coordination number

atomic packing factor (APF)

Two other important characteristics of a crystal structure are the **coordination number** and the **atomic packing factor (APF)**. For metals, each atom has the same number of nearest-neighbor or touching atoms, which is the coordination number. For face-centered cubics, the coordination number is 12. This may be confirmed by examination of Figure 3.1a; the front face atom has four corner nearest-neighbor atoms surrounding it, four face atoms that are in contact from behind, and four other equivalent face atoms residing in the next unit cell to the front, which is not shown.

The APF is the sum of the sphere volumes of all atoms within a unit cell (assuming the atomic hard sphere model) divided by the unit cell volume—that is

Definition of atomic packing factor

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} \quad (3.2)$$

For the FCC structure, the atomic packing factor is 0.74, which is the maximum packing possible for spheres all having the same diameter. Computation of this APF is also included as an example problem. Metals typically have relatively large atomic packing factors to maximize the shielding provided by the free electron cloud.

The Body-Centered Cubic Crystal Structure

body-centered cubic (BCC)

Another common metallic crystal structure also has a cubic unit cell with atoms located at all eight corners and a single atom at the cube center. This is called a **body-centered cubic (BCC)** crystal structure. A collection of spheres depicting this crystal structure is shown in Figure 3.2c, whereas Figures 3.2a and 3.2b are diagrams of BCC unit cells with the atoms represented by hard sphere and reduced-sphere models, respectively. Center and corner atoms touch one another along cube diagonals, and unit cell length a and atomic radius R are related through

Unit cell edge length for body-centered cubic

$$a = \frac{4R}{\sqrt{3}} \quad (3.3)$$

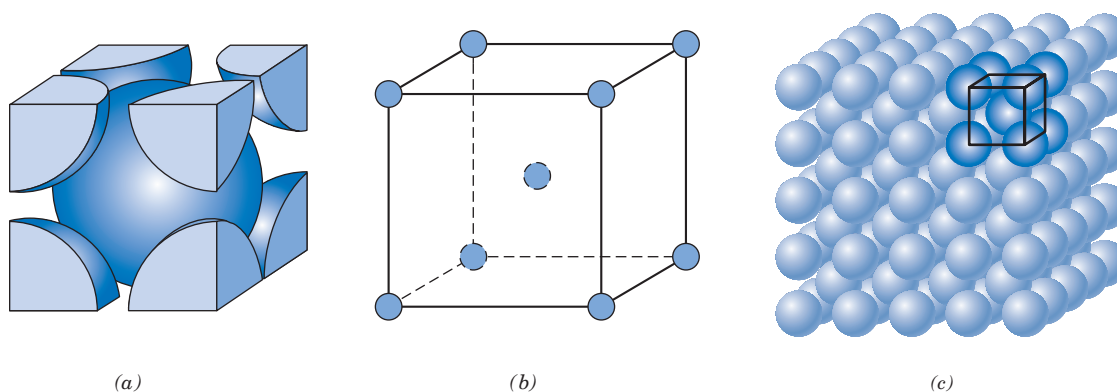


Figure 3.2 For the body-centered cubic crystal structure, (a) a hard sphere unit cell representation, (b) a reduced-sphere unit cell, and (c) an aggregate of many atoms. [Figure (c) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

3.4 Metallic Crystal Structures • 43

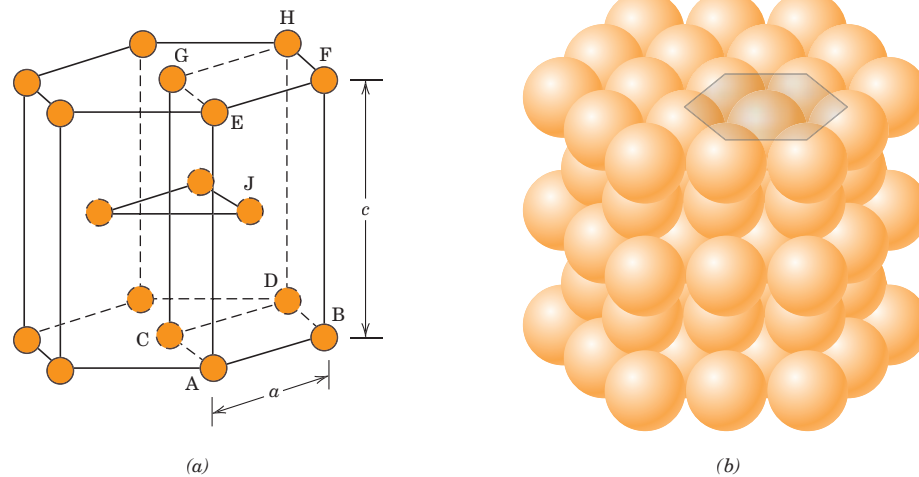


Figure 3.3 For the hexagonal close-packed crystal structure, (a) a reduced-sphere unit cell (a and c represent the short and long edge lengths, respectively), and (b) an aggregate of many atoms. [Figure (b) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

Chromium, iron, tungsten, as well as several other metals listed in Table 3.1 exhibit a BCC structure.

Two atoms are associated with each BCC unit cell: the equivalent of one atom from the eight corners, each of which is shared among eight unit cells, and the single center atom, which is wholly contained within its cell. In addition, corner and center atom positions are equivalent. The coordination number for the BCC crystal structure is 8; each center atom has as nearest neighbors its eight corner atoms. Since the coordination number is less for BCC than FCC, so also is the atomic packing factor for BCC lower—0.68 versus 0.74.

The Hexagonal Close-Packed Crystal Structure

Not all metals have unit cells with cubic symmetry; the final common metallic crystal structure to be discussed has a unit cell that is hexagonal. Figure 3.3a shows a reduced-sphere unit cell for this structure, which is termed **hexagonal close-packed (HCP)**; an assemblage of several HCP unit cells is presented in Figure 3.3b.¹ The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes. The atoms in this midplane have as nearest neighbors atoms in both of the adjacent two planes. The equivalent of six atoms is contained in each unit cell; one-sixth of each of the 12 top and bottom face corner atoms, one-half of each of the 2 center face atoms, and all 3 midplane interior atoms. If a and c represent, respectively, the short and long unit cell dimensions of Figure 3.3a, the c/a ratio should be 1.633; however, for some HCP metals this ratio deviates from the ideal value.

¹ Alternatively, the unit cell for HCP may be specified in terms of the parallelepiped defined by atoms labeled A through H in Figure 3.3a. As such, the atom denoted J lies within the unit cell interior.

Crystal Systems and
Unit Cells for Metals

hexagonal close-
packed (HCP)

Crystal Systems and
Unit Cells for Metals

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The coordination number and the atomic packing factor for the HCP crystal structure are the same as for FCC: 12 and 0.74, respectively. The HCP metals include cadmium, magnesium, titanium, and zinc; some of these are listed in Table 3.1.

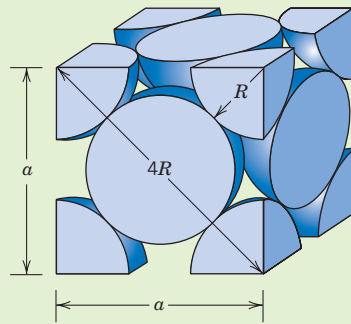
EXAMPLE PROBLEM 3.1

Determination of FCC Unit Cell Volume

Calculate the volume of an FCC unit cell in terms of the atomic radius R .

Solution

In the FCC unit cell illustrated,



the atoms touch one another across a face-diagonal the length of which is $4R$. Since the unit cell is a cube, its volume is a^3 , where a is the cell edge length. From the right triangle on the face,

$$a^2 + a^2 = (4R)^2$$

or, solving for a ,

$$a = 2R\sqrt{2} \quad (3.1)$$

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2} \quad (3.4)$$

EXAMPLE PROBLEM 3.2

Computation of the Atomic Packing Factor for FCC

Show that the atomic packing factor for the FCC crystal structure is 0.74.

Solution

The APF is defined as the fraction of solid sphere volume in a unit cell, or

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_S}{V_C}$$

Both the total atom and unit cell volumes may be calculated in terms of the atomic radius R . The volume for a sphere is $\frac{4}{3}\pi R^3$, and since there are four

3.5 Density Computations • 45

atoms per FCC unit cell, the total FCC atom (or sphere) volume is

$$V_S = (4)\frac{4}{3}\pi R^3 = \frac{16}{3}\pi R^3$$

From Example Problem 3.1, the total unit cell volume is

$$V_C = 16R^3\sqrt{2}$$

Therefore, the atomic packing factor is

$$\text{APF} = \frac{V_S}{V_C} = \frac{(\frac{16}{3})\pi R^3}{16R^3\sqrt{2}} = 0.74$$

3.5 DENSITY COMPUTATIONS

A knowledge of the crystal structure of a metallic solid permits computation of its theoretical density ρ through the relationship

Theoretical density
for metals

$$\rho = \frac{nA}{V_C N_A} \quad (3.5)$$

where

n = number of atoms associated with each unit cell

A = atomic weight

V_C = volume of the unit cell

N_A = Avogadro's number (6.023×10^{23} atoms/mol)

EXAMPLE PROBLEM 3.3

Theoretical Density Computation for Copper

Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its theoretical density and compare the answer with its measured density.

Solution

Equation 3.5 is employed in the solution of this problem. Since the crystal structure is FCC, n , the number of atoms per unit cell, is 4. Furthermore, the atomic weight A_{Cu} is given as 63.5 g/mol. The unit cell volume V_C for FCC was determined in Example Problem 3.1 as $16R^3\sqrt{2}$, where R , the atomic radius, is 0.128 nm.

Substitution for the various parameters into Equation 3.5 yields

$$\begin{aligned} \rho &= \frac{nA_{\text{Cu}}}{V_C N_A} = \frac{nA_{\text{Cu}}}{(16R^3\sqrt{2})N_A} \\ &= \frac{(4 \text{ atoms/unit cell})(63.5 \text{ g/mol})}{[16\sqrt{2}(1.28 \times 10^{-8} \text{ cm})^3/\text{unit cell}](6.023 \times 10^{23} \text{ atoms/mol})} \\ &= 8.89 \text{ g/cm}^3 \end{aligned}$$

The literature value for the density of copper is 8.94 g/cm^3 , which is in very close agreement with the foregoing result.

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3.6 POLYMORPHISM AND ALLOTROPY

polymorphism

allotropy

Some metals, as well as nonmetals, may have more than one crystal structure, a phenomenon known as **polymorphism**. When found in elemental solids, the condition is often termed **allotropy**. The prevailing crystal structure depends on both the temperature and the external pressure. One familiar example is found in carbon: graphite is the stable polymorph at ambient conditions, whereas diamond is formed at extremely high pressures. Also, pure iron has a BCC crystal structure at room temperature, which changes to FCC iron at 912°C (1674°F). Most often a modification of the density and other physical properties accompanies a polymorphic transformation.

3.7 CRYSTAL SYSTEMS



Crystal Systems and Unit Cells for Metals

lattice parameters

crystal system

Since there are many different possible crystal structures, it is sometimes convenient to divide them into groups according to unit cell configurations and/or atomic arrangements. One such scheme is based on the unit cell geometry, that is, the shape of the appropriate unit cell parallelepiped without regard to the atomic positions in the cell. Within this framework, an x, y, z coordinate system is established with its origin at one of the unit cell corners; each of the x, y , and z axes coincides with one of the three parallelepiped edges that extend from this corner, as illustrated in Figure 3.4. The unit cell geometry is completely defined in terms of six parameters: the three edge lengths a, b , and c , and the three interaxial angles α, β , and γ . These are indicated in Figure 3.4, and are sometimes termed the **lattice parameters** of a crystal structure.

On this basis there are seven different possible combinations of a, b , and c , and α, β , and γ , each of which represents a distinct **crystal system**. These seven crystal systems are cubic, tetragonal, hexagonal, orthorhombic, rhombohedral,² monoclinic, and triclinic. The lattice parameter relationships and unit cell sketches for each are represented in Table 3.2. The cubic system, for which $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$, has the greatest degree of symmetry. Least symmetry is displayed by the triclinic system, since $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$.

From the discussion of metallic crystal structures, it should be apparent that both FCC and BCC structures belong to the cubic crystal system, whereas HCP falls within hexagonal. The conventional hexagonal unit cell really consists of three parallelepipeds situated as shown in Table 3.2.

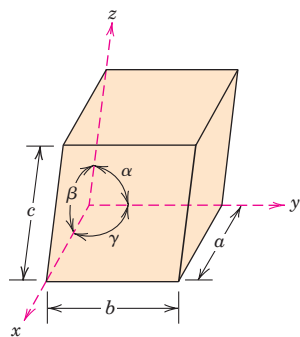
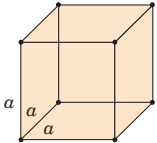
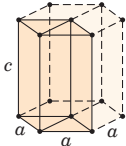
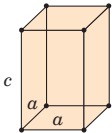
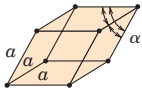
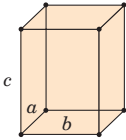
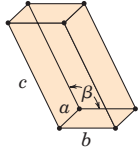
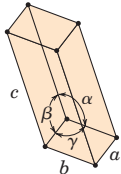


Figure 3.4 A unit cell with x, y , and z coordinate axes, showing axial lengths (a, b , and c) and interaxial angles (α, β , and γ).

² Also called trigonal.

3.7 Crystal Systems • 47

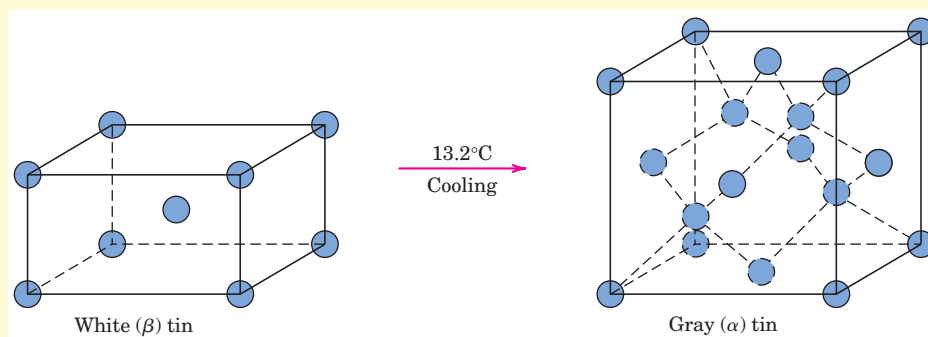
Table 3.2 Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

<i>Crystal System</i>	<i>Axial Relationships</i>	<i>Interaxial Angles</i>	<i>Unit Cell Geometry</i>
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

MATERIAL OF IMPORTANCE**Tin (Its Allotropic Transformation)**

Another common metal that experiences an allotropic change is tin. White (or β) tin, having a body-centered tetragonal crystal structure at room temperature, transforms, at 13.2°C (55.8°F),

to gray (or α) tin, which has a crystal structure similar to diamond (i.e., the diamond cubic crystal structure); this transformation is represented schematically as follows:



The rate at which this change takes place is extremely slow; however, the lower the temperature (below 13.2°C) the faster the rate. Accompanying this white tin-to-gray tin transformation is an increase in volume (27 percent), and, accordingly, a decrease in density (from 7.30 g/cm³ to 5.77 g/cm³). Consequently, this volume expansion results in the disintegration of the white tin metal into a coarse powder of the gray allotrope. For normal subambient temperatures, there is no need to worry about this disintegration process for tin products, due to the very slow rate at which the transformation occurs.

This white-to-gray-tin transition produced some rather dramatic results in 1850 in Russia. The winter that year was particularly cold, and record low temperatures persisted for extended periods of time. The uniforms of some Russian soldiers had tin buttons, many of which crumbled due to these extreme cold conditions, as did also many of the tin church organ pipes. This problem came to be known as the “tin disease.”



Specimen of white tin (left). Another specimen disintegrated upon transforming to gray tin (right) after it was cooled to and held at a temperature below 13.2°C for an extended period of time.

(Photograph courtesy of Professor Bill Plumbridge, Department of Materials Engineering, The Open University, Milton Keynes, England.)

3.8 Point Coordinates • 49

**Concept Check 3.1**

What is the difference between crystal structure and crystal system?

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

It is important to note that many of the principles and concepts addressed in previous discussions in this chapter also apply to crystalline ceramic and polymeric systems (Chapters 12 and 14). For example, crystal structures are most often described in terms of unit cells, which are normally more complex than those for FCC, BCC, and HCP. In addition, for these other systems, we are often interested in determining atomic packing factors and densities, using modified forms of Equations 3.2 and 3.5. Furthermore, according to unit cell geometry, crystal structures of these other material types are grouped within the seven crystal systems.

Crystallographic Points, Directions, and Planes

When dealing with crystalline materials, it often becomes necessary to specify a particular point within a unit cell, a crystallographic direction, or some crystallographic plane of atoms. Labeling conventions have been established in which three numbers or indices are used to designate point locations, directions, and planes. The basis for determining index values is the unit cell, with a right-handed coordinate system consisting of three (x , y , and z) axes situated at one of the corners and coinciding with the unit cell edges, as shown in Figure 3.4. For some crystal systems—namely, hexagonal, rhombohedral, monoclinic, and triclinic—the three axes are *not* mutually perpendicular, as in the familiar Cartesian coordinate scheme.

3.8 POINT COORDINATES

The position of any point located within a unit cell may be specified in terms of its coordinates as fractional multiples of the unit cell edge lengths (i.e., in terms of a , b , and c). To illustrate, consider the unit cell and the point P situated therein as shown in Figure 3.5. We specify the position of P in terms of the generalized coordinates

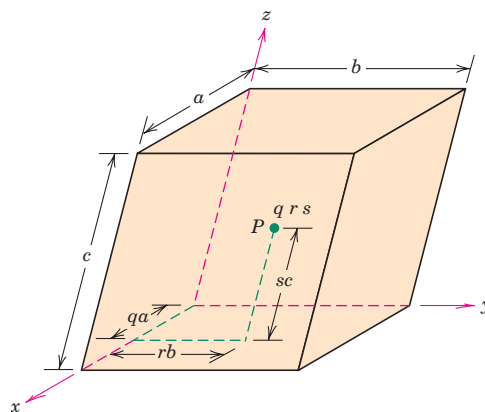


Figure 3.5 The manner in which the q , r , and s coordinates at point P within the unit cell are determined. The q coordinate (which is a fraction) corresponds to the distance qa along the x axis, where a is the unit cell edge length. The respective r and s coordinates for the y and z axes are determined similarly.

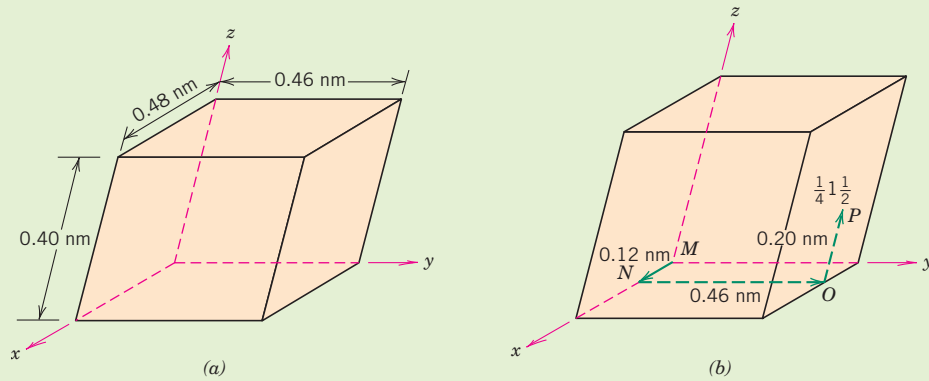
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q , r , and s where q is some fractional length of a along the x axis, r is some fractional length of b along the y axis, and similarly for s . Thus, the position of P is designated using coordinates $q\ r\ s$ with values that are less than or equal to unity. Furthermore, we have chosen not to separate these coordinates by commas or any other punctuation marks (which is the normal convention).

EXAMPLE PROBLEM 3.4

Location of Point Having Specified Coordinates

For the unit cell shown in the accompanying sketch (a), locate the point having coordinates $\frac{1}{4}\ 1\ \frac{1}{2}$.



Solution

From sketch (a), edge lengths for this unit cell are as follows: $a = 0.48$ nm, $b = 0.46$ nm, and $c = 0.40$ nm. Furthermore, in light of the above discussion, fractional lengths are $q = \frac{1}{4}$, $r = 1$, and $s = \frac{1}{2}$. Therefore, first we move from the origin of the unit cell (point M) $qa = \frac{1}{4}(0.48 \text{ nm}) = 0.12$ nm units along the x axis (to point N), as shown in the (b) sketch. Similarly, we proceed $rb = (1)(0.46 \text{ nm}) = 0.46$ nm parallel to the y axis, from point N to point O . Finally, we move from this position, $sc = \frac{1}{2}(0.40 \text{ nm}) = 0.20$ nm units parallel to the z axis to point P as noted again in sketch (b). This point P then corresponds to the $\frac{1}{4}\ 1\ \frac{1}{2}$ point coordinates.

EXAMPLE PROBLEM 3.5

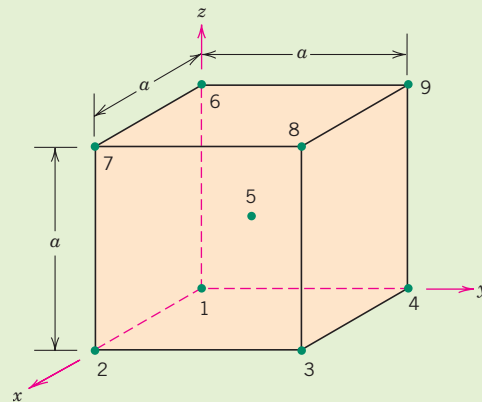
Specification of Point Coordinates

Specify point coordinates for all atom positions for a BCC unit cell.

Solution

For the BCC unit cell of Figure 3.2, atom position coordinates correspond to the locations of the centers of all atoms in the unit cell—that is, the eight corner atoms and single center atom. These positions are noted (and also numbered) in the following figure.

3.9 Crystallographic Directions • 51



Point coordinates for position number 1 are 0 0 0; this position is located at the origin of the coordinate system, and, as such, the fractional unit cell edge lengths along the x , y , and z axes are, respectively, $0a$, $0a$, and $0a$. Furthermore, for position number 2, since it lies one unit cell edge length along the x axis, its fractional edge lengths are a , $0a$, and $0a$, respectively, which yield point coordinates of 1 0 0. The following table presents fractional unit cell lengths along the x , y , and z axes, and their corresponding point coordinates for each of the nine points in the above figure.

Point Number	Fractional Lengths			Point Coordinates
	x axis	y axis	z axis	
1	0	0	0	0 0 0
2	1	0	0	1 0 0
3	1	1	0	1 1 0
4	0	1	0	0 1 0
5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2} \frac{1}{2} \frac{1}{2}$
6	0	0	1	0 0 1
7	1	0	1	1 0 1
8	1	1	1	1 1 1
9	0	1	1	0 1 1

3.9 CRYSTALLOGRAPHIC DIRECTIONS

A crystallographic direction is defined as a line between two points, or a vector. The following steps are utilized in the determination of the three directional indices:



Crystallographic
Directions

1. A vector of convenient length is positioned such that it passes through the origin of the coordinate system. Any vector may be translated throughout the crystal lattice without alteration, if parallelism is maintained.
2. The length of the vector projection on each of the three axes is determined; *these are measured in terms of the unit cell dimensions a , b , and c .*
3. These three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values.
4. The three indices, not separated by commas, are enclosed in square brackets, thus: $[uvw]$. The u , v , and w integers correspond to the reduced projections along the x , y , and z axes, respectively.

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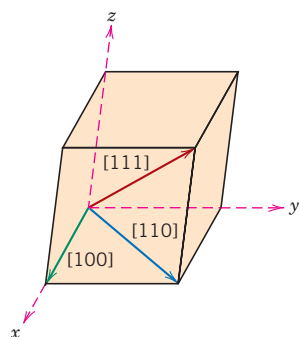


Figure 3.6 The $[100]$, $[110]$, and $[111]$ directions within a unit cell.

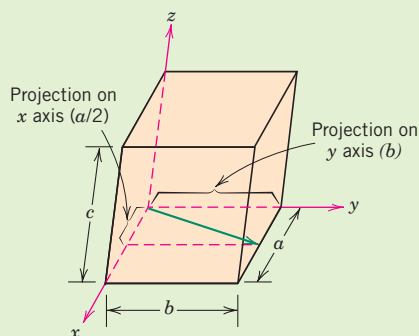
For each of the three axes, there will exist both positive and negative coordinates. Thus negative indices are also possible, which are represented by a bar over the appropriate index. For example, the $[\bar{1}11]$ direction would have a component in the $-y$ direction. Also, changing the signs of all indices produces an antiparallel direction; that is, $[\bar{1}\bar{1}\bar{1}]$ is directly opposite to $[111]$. If more than one direction (or plane) is to be specified for a particular crystal structure, it is imperative for the maintaining of consistency that a positive–negative convention, once established, not be changed.

The $[100]$, $[110]$, and $[111]$ directions are common ones; they are drawn in the unit cell shown in Figure 3.6.

EXAMPLE PROBLEM 3.6

Determination of Directional Indices

Determine the indices for the direction shown in the accompanying figure.



Solution

The vector, as drawn, passes through the origin of the coordinate system, and therefore no translation is necessary. Projections of this vector onto the x , y , and z axes are, respectively, $a/2$, b , and $0c$, which become $\frac{1}{2}$, 1 , and 0 in terms of the unit cell parameters (i.e., when the a , b , and c are dropped). Reduction of these numbers to the lowest set of integers is accompanied by multiplication of each by the factor 2. This yields the integers 1, 2, and 0, which are then enclosed in brackets as $[120]$.

3.9 Crystallographic Directions • 53

This procedure may be summarized as follows:

	x	y	z
Projections	$a/2$	b	$0c$
Projections (in terms of a , b , and c)	$\frac{1}{2}$	1	0
Reduction	1	2	0
Enclosure	$[120]$		

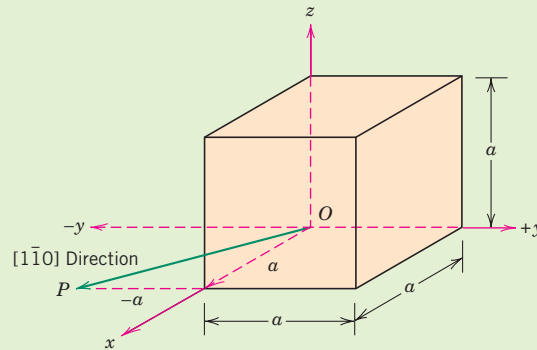
EXAMPLE PROBLEM 3.7

Construction of Specified Crystallographic Direction

Draw a $[1\bar{1}0]$ direction within a cubic unit cell.

Solution

First construct an appropriate unit cell and coordinate axes system. In the accompanying figure the unit cell is cubic, and the origin of the coordinate system, point O , is located at one of the cube corners.



This problem is solved by reversing the procedure of the preceding example. For this $[1\bar{1}0]$ direction, the projections along the x , y , and z axes are a , $-a$, and $0a$, respectively. This direction is defined by a vector passing from the origin to point P , which is located by first moving along the x axis a units, and from this position, parallel to the y axis $-a$ units, as indicated in the figure. There is no z component to the vector, since the z projection is zero.

For some crystal structures, several nonparallel directions with different indices are actually equivalent; this means that the spacing of atoms along each direction is the same. For example, in cubic crystals, all the directions represented by the following indices are equivalent: $[100]$, $[\bar{1}00]$, $[010]$, $[0\bar{1}0]$, $[001]$, and $[00\bar{1}]$. As a convenience, equivalent directions are grouped together into a *family*, which are enclosed in angle brackets, thus: $\langle 100 \rangle$. Furthermore, directions in cubic crystals having the same indices without regard to order or sign, for example, $[123]$ and $[\bar{2}1\bar{3}]$, are equivalent. This is, in general, not true for other crystal systems. For example, for crystals of tetragonal symmetry, $[100]$ and $[010]$ directions are equivalent, whereas $[100]$ and $[001]$ are not.

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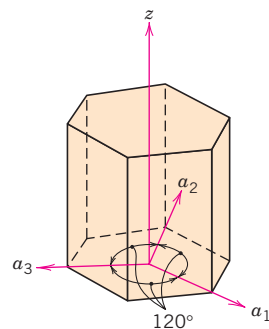


Figure 3.7 Coordinate axis system for a hexagonal unit cell (Miller-Bravais scheme).

Hexagonal Crystals

A problem arises for crystals having hexagonal symmetry in that some crystallographic equivalent directions will not have the same set of indices. This is circumvented by utilizing a four-axis, or *Miller-Bravais*, coordinate system as shown in Figure 3.7. The three a_1 , a_2 , and a_3 axes are all contained within a single plane (called the basal plane) and are at 120° angles to one another. The z axis is perpendicular to this basal plane. Directional indices, which are obtained as described above, will be denoted by four indices, as $[uvtw]$; by convention, the first three indices pertain to projections along the respective a_1 , a_2 , and a_3 axes in the basal plane.

Conversion from the three-index system to the four-index system,

$$[u'v'w'] \longrightarrow [uvtw]$$

is accomplished by the following formulas:

$$u = \frac{1}{3}(2u' - v') \quad (3.6a)$$

$$v = \frac{1}{3}(2v' - u') \quad (3.6b)$$

$$t = -(u + v) \quad (3.6c)$$

$$w = w' \quad (3.6d)$$

where primed indices are associated with the three-index scheme and unprimed with the new Miller-Bravais four-index system. (Of course, reduction to the lowest set of integers may be necessary, as discussed above.) For example, the $[010]$ direction becomes $[\bar{1}2\bar{1}0]$. Several different directions are indicated in the hexagonal unit cell (Figure 3.8a).

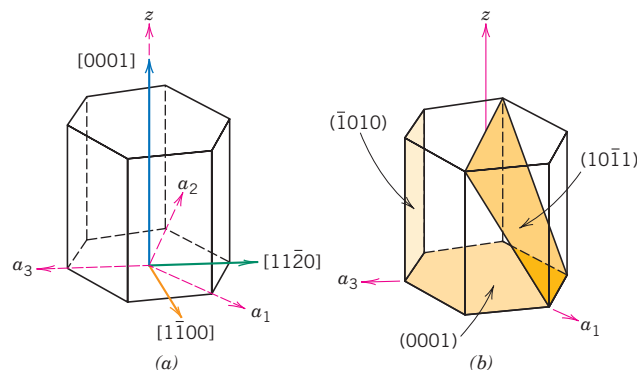


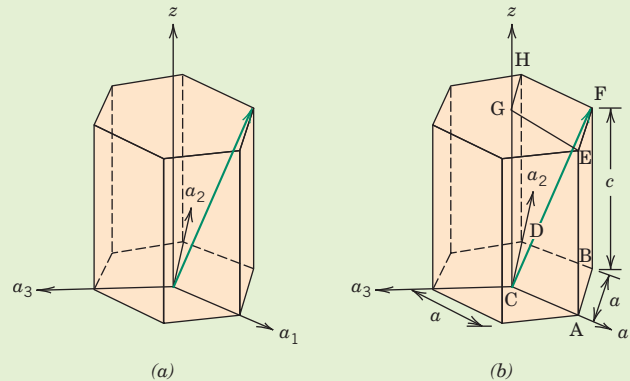
Figure 3.8 For the hexagonal crystal system, (a) $[0001]$, $[1100]$, and $[1120]$ directions, and (b) the (0001) , $(10\bar{1}1)$, and $(\bar{1}010)$ planes.

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EXAMPLE PROBLEM 3.8

Determination of Directional Indices for a Hexagonal Unit Cell

Determine the indices for the direction shown in the hexagonal unit cell of sketch (a) below.

**Solution**

In sketch (b), one of the three parallelepipeds comprising the hexagonal cell is delineated—its corners are labeled with letters A through H, with the origin of the a_1 - a_2 - a_3 - z axes coordinate system located at the corner labeled C. We use this unit cell as a reference for specifying the directional indices. It now becomes necessary to determine projections of the direction vector on the a_1 , a_2 , and z axes. These respective projections are a (a_1 axis), a (a_2 axis) and c (z axis), which become 1, 1, and 1 in terms of the unit cell parameters. Thus,

$$u' = 1 \quad v' = 1 \quad w' = 1$$

Also, from Equations 3.6a, 3.6b, 3.6c, and 3.6d

$$u = \frac{1}{3}(2u' - v') = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

$$v = \frac{1}{3}(2v' - u') = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

$$t = -(u + v) = -\left(\frac{1}{3} + \frac{1}{3}\right) = -\frac{2}{3}$$

$$w = w' = 1$$

Multiplication of the above indices by 3 reduces them to the lowest set, which yields values for u , v , t , and w of 1, 1, -2 and 3, respectively. Hence, the direction shown in the figure is $[11\bar{2}3]$.

3.10 CRYSTALLOGRAPHIC PLANES

The orientations of planes for a crystal structure are represented in a similar manner. Again, the unit cell is the basis, with the three-axis coordinate system as represented in Figure 3.4. In all but the hexagonal crystal system, crystallographic planes are specified by three **Miller indices** as (hkl) . Any two planes parallel to each other

Miller indices

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are equivalent and have identical indices. The procedure employed in determination of the h , k , and l index numbers is as follows:



Crystallographic
Planes

1. If the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.
2. At this point the crystallographic plane either intersects or parallels each of the three axes; the length of the planar intercept for each axis is determined in terms of the lattice parameters a , b , and c .
3. The reciprocals of these numbers are taken. A plane that parallels an axis may be considered to have an infinite intercept, and, therefore, a zero index.
4. If necessary, these three numbers are changed to the set of smallest integers by multiplication or division by a common factor.³
5. Finally, the integer indices, not separated by commas, are enclosed within parentheses, thus: (hkl) .

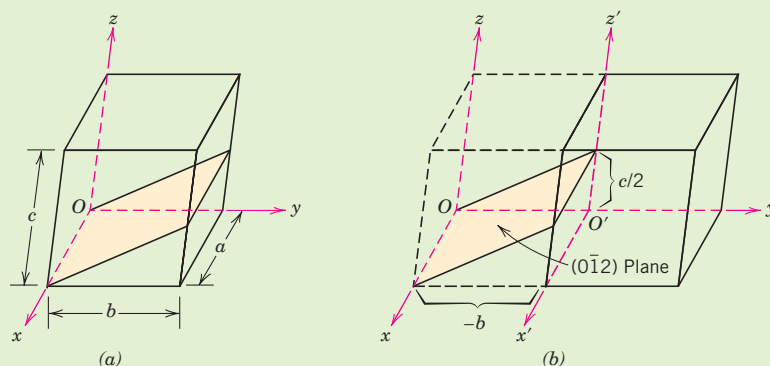
An intercept on the negative side of the origin is indicated by a bar or minus sign positioned over the appropriate index. Furthermore, reversing the directions of all indices specifies another plane parallel to, on the opposite side of and equidistant from, the origin. Several low-index planes are represented in Figure 3.9.

One interesting and unique characteristic of cubic crystals is that planes and directions having the same indices are perpendicular to one another; however, for other crystal systems there are no simple geometrical relationships between planes and directions having the same indices.

EXAMPLE PROBLEM 3.9

Determination of Planar (Miller) Indices

Determine the Miller indices for the plane shown in the accompanying sketch (a).



³ On occasion, index reduction is not carried out (e.g., for x-ray diffraction studies that are described in Section 3.16); for example, (002) is not reduced to (001) . In addition, for ceramic materials, the ionic arrangement for a reduced-index plane may be different from that for a nonreduced one.

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Solution

Since the plane passes through the selected origin O , a new origin must be chosen at the corner of an adjacent unit cell, taken as O' and shown in sketch (b). This plane is parallel to the x axis, and the intercept may be taken as ∞a . The y and z axes intersections, referenced to the new origin O' , are $-b$ and $c/2$, respectively. Thus, in terms of the lattice parameters a , b , and c , these intersections are ∞ , -1 , and $\frac{1}{2}$. The reciprocals of these numbers are 0, -1 , and 2; and since all are integers, no further reduction is necessary. Finally, enclosure in parentheses yields $(0\bar{1}2)$.

These steps are briefly summarized below:

	x	y	z
Intercepts	∞a	$-b$	$c/2$
Intercepts (in terms of lattice parameters)	∞	-1	$\frac{1}{2}$
Reciprocals	0	-1	2
Reductions (unnecessary)			
Enclosure		$(0\bar{1}2)$	

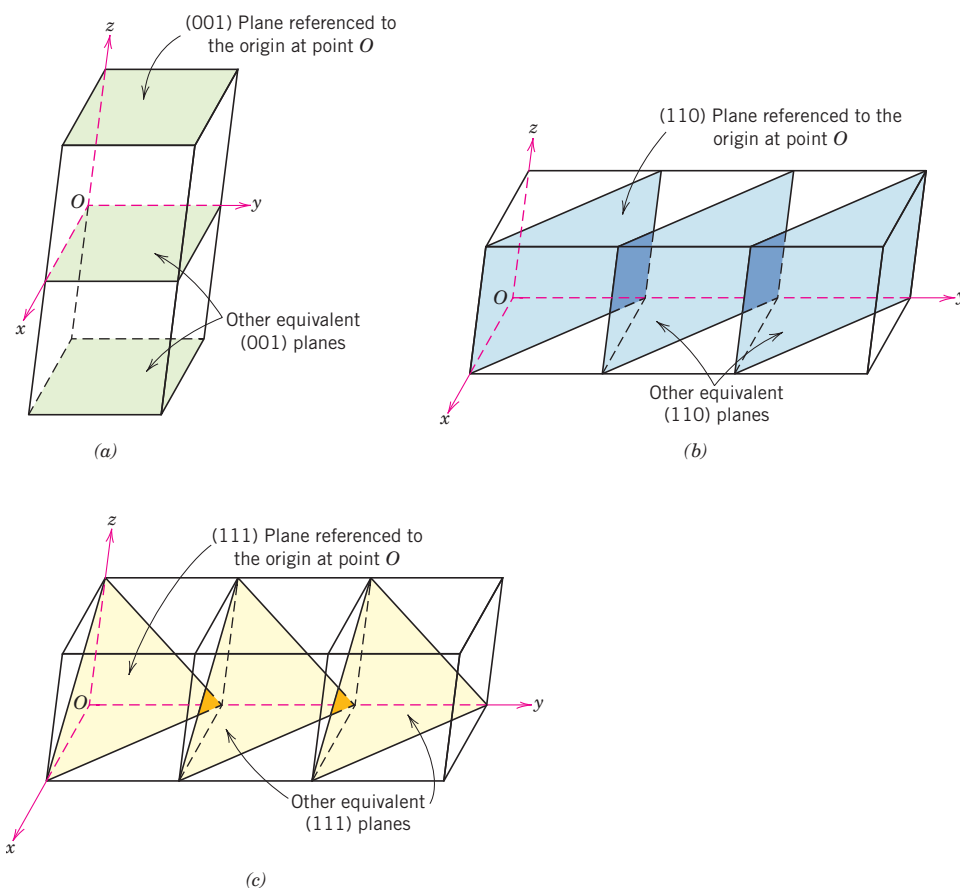
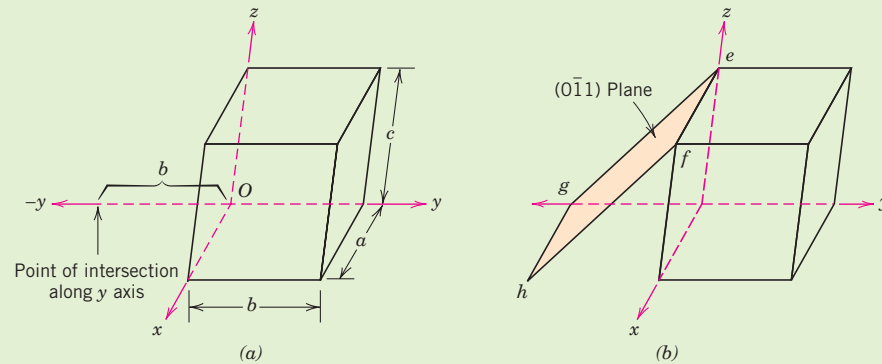


Figure 3.9 Representations of a series each of (a) (001), (b) (110), and (c) (111) crystallographic planes.

EXAMPLE PROBLEM 3.10**Construction of Specified Crystallographic Plane**

Construct a $(0\bar{1}1)$ plane within a cubic unit cell.

**Solution**

To solve this problem, carry out the procedure used in the preceding example in reverse order. To begin, the indices are removed from the parentheses, and reciprocals are taken, which yields ∞ , -1 , and 1 . This means that the particular plane parallels the x axis while intersecting the y and z axes at $-b$ and c , respectively, as indicated in the accompanying sketch (a). This plane has been drawn in sketch (b). A plane is indicated by lines representing its intersections with the planes that constitute the faces of the unit cell or their extensions. For example, in this figure, line ef is the intersection between the $(0\bar{1}1)$ plane and the top face of the unit cell; also, line gh represents the intersection between this same $(0\bar{1}1)$ plane and the plane of the bottom unit cell face extended. Similarly, lines eg and fh are the intersections between $(0\bar{1}1)$ and back and front cell faces, respectively.

Atomic Arrangements

Planar Atomic Arrangements

The atomic arrangement for a crystallographic plane, which is often of interest, depends on the crystal structure. The (110) atomic planes for FCC and BCC crystal structures are represented in Figures 3.10 and 3.11; reduced-sphere unit cells are also included. Note that the atomic packing is different for each case. The circles represent atoms lying in the crystallographic planes as would be obtained from a slice taken through the centers of the full-sized hard spheres.

A “family” of planes contains all those planes that are crystallographically equivalent—that is, having the same atomic packing; and a family is designated by

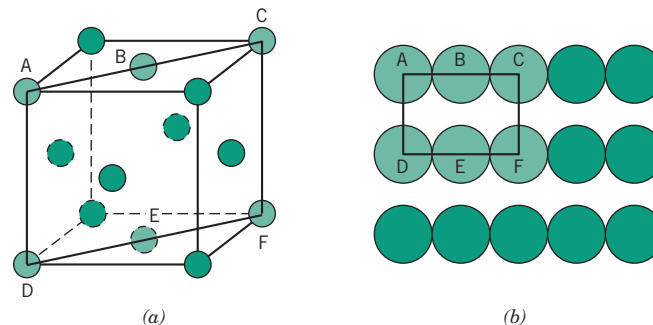
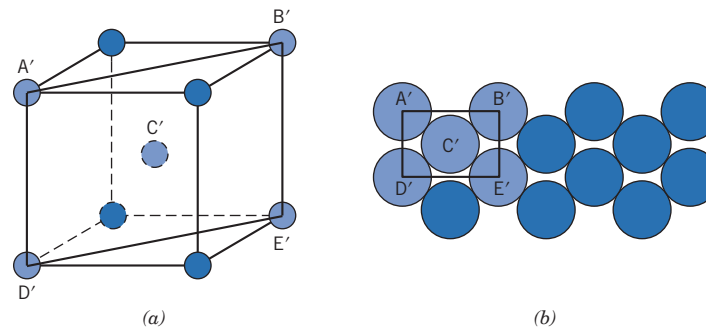


Figure 3.10 (a) Reduced-sphere FCC unit cell with (110) plane. (b) Atomic packing of an FCC (110) plane. Corresponding atom positions from (a) are indicated.

3.10 Crystallographic Planes • 59

**Figure 3.11**

(a) Reduced-sphere BCC unit cell with (110) plane.
 (b) Atomic packing of a BCC (110) plane. Corresponding atom positions from (a) are indicated.

indices that are enclosed in braces—such as $\{100\}$. For example, in cubic crystals the (111) , $(\bar{1}11)$, $(1\bar{1}1)$, $(11\bar{1})$, $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$, and $(11\bar{1})$ planes all belong to the $\{111\}$ family. On the other hand, for tetragonal crystal structures, the $\{100\}$ family would contain only the (100) , $(\bar{1}00)$, (010) , and $(0\bar{1}0)$ since the (001) and $(00\bar{1})$ planes are not crystallographically equivalent. Also, in the cubic system only, planes having the same indices, irrespective of order and sign, are equivalent. For example, both (123) and $(3\bar{1}2)$ belong to the $\{123\}$ family.

Hexagonal Crystals

For crystals having hexagonal symmetry, it is desirable that equivalent planes have the same indices; as with directions, this is accomplished by the Miller–Bravais system shown in Figure 3.7. This convention leads to the four-index $(hkil)$ scheme, which is favored in most instances, since it more clearly identifies the orientation of a plane in a hexagonal crystal. There is some redundancy in that i is determined by the sum of h and k through

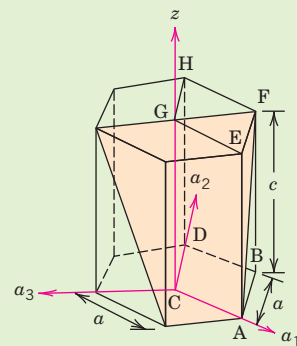
$$i = -(h + k) \quad (3.7)$$

Otherwise the three h , k , and l indices are identical for both indexing systems. Figure 3.8b presents several of the common planes that are found for crystals having hexagonal symmetry.

EXAMPLE PROBLEM 3.11

Determination of Miller–Bravais Indices for a Plane Within a Hexagonal Unit Cell

Determine the Miller–Bravais indices for the plane shown in the hexagonal unit cell.



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Solution

To determine these Miller–Bravais indices, consider the plane in the figure referenced to the parallelepiped labeled with the letters A through H at its corners. This plane intersects the a_1 axis at a distance a from the origin of the a_1 – a_2 – a_3 – z coordinate axes system (point C). Furthermore, its intersections with the a_2 and z axes are $-a$ and c , respectively. Therefore, in terms of the lattice parameters, these intersections are 1, -1 , and 1. Furthermore, the reciprocals of these numbers are also 1, -1 , and 1. Hence

$$h = 1$$

$$k = -1$$

$$l = 1$$

and, from Equation 3.7

$$\begin{aligned} i &= -(h + k) \\ &= -(1 - 1) = 0 \end{aligned}$$

Therefore the (hkl) indices are $(1\bar{1}0)$.

Notice that the third index is zero (i.e., its reciprocal $= \infty$), which means that this plane parallels the a_3 axis. Upon inspection of the above figure, it may be noted that this is indeed the case.

3.11 LINEAR AND PLANAR DENSITIES

The two previous sections discussed the equivalency of nonparallel crystallographic directions and planes. Directional equivalency is related to *linear density* in the sense that, for a particular material, equivalent directions have identical linear densities. The corresponding parameter for crystallographic planes is *planar density*, and planes having the same planar density values are also equivalent.

Linear density (LD) is defined as the number of atoms per unit length whose centers lie on the direction vector for a specific crystallographic direction; that is,

$$\text{LD} = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}} \quad (3.8)$$

Of course, the units of linear density are reciprocal length (e.g., nm^{-1} , m^{-1}).

For example, let us determine the linear density of the $[110]$ direction for the FCC crystal structure. An FCC unit cell (reduced sphere) and the $[110]$ direction therein are shown in Figure 3.12a. Represented in Figure 3.12b are those five atoms that lie on the bottom face of this unit cell; here the $[110]$ direction vector passes from the center of atom X, through atom Y, and finally to the center of atom Z. With regard to the numbers of atoms, it is necessary to take into account the sharing of atoms with adjacent unit cells (as discussed in Section 3.4 relative to atomic packing factor computations). Each of the X and Z corner atoms are also shared with one other adjacent unit cell along this $[110]$ direction (i.e., one-half of each of these atoms belongs to the unit cell being considered), while atom Y lies entirely within the unit cell. Thus, there is an equivalence of two atoms along the $[110]$ direction vector in the unit cell. Now, the direction vector length is equal to $4R$ (Figure 3.12b); thus, from Equation 3.8, the $[110]$ linear density for FCC is

$$\text{LD}_{110} = \frac{2 \text{ atoms}}{4R} = \frac{1}{2R} \quad (3.9)$$

3.12 Close-Packed Crystal Structures • 61

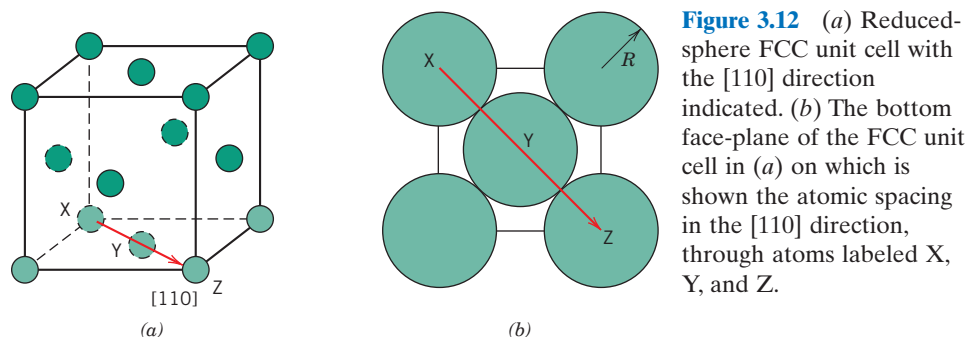


Figure 3.12 (a) Reduced-sphere FCC unit cell with the [110] direction indicated. (b) The bottom face-plane of the FCC unit cell in (a) on which is shown the atomic spacing in the [110] direction, through atoms labeled X, Y, and Z.

In an analogous manner, planar density (PD) is taken as the number of atoms per unit area that are centered on a particular crystallographic plane, or

$$PD = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}} \quad (3.10)$$

The units for planar density are reciprocal area (e.g., nm^{-2} , m^{-2}).

For example, consider the section of a (110) plane within an FCC unit cell as represented in Figures 3.10a and 3.10b. Although six atoms have centers that lie on this plane (Figure 3.10b), only one-quarter of each of atoms A, C, D, and F, and one-half of atoms B and E, for a total equivalence of just 2 atoms are on that plane. Furthermore, the area of this rectangular section is equal to the product of its length and width. From Figure 3.10b, the length (horizontal dimension) is equal to $4R$, whereas the width (vertical dimension) is equal to $2R\sqrt{2}$, since it corresponds to the FCC unit cell edge length (Equation 3.1). Thus, the area of this planar region is $(4R)(2R\sqrt{2}) = 8R^2\sqrt{2}$, and the planar density is determined as follows:

$$PD_{110} = \frac{2 \text{ atoms}}{8R^2\sqrt{2}} = \frac{1}{4R^2\sqrt{2}} \quad (3.11)$$

Linear and planar densities are important considerations relative to the process of slip—that is, the mechanism by which metals plastically deform (Section 7.4). Slip occurs on the most densely packed crystallographic planes and, in those planes, along directions having the greatest atomic packing.

3.12 CLOSE-PACKED CRYSTAL STRUCTURES



Close-Packed Structures (Metals)

You may remember from the discussion on metallic crystal structures that both face-centered cubic and hexagonal close-packed crystal structures have atomic packing factors of 0.74, which is the most efficient packing of equal-sized spheres or atoms. In addition to unit cell representations, these two crystal structures may be described in terms of close-packed planes of atoms (i.e., planes having a maximum atom or sphere-packing density); a portion of one such plane is illustrated in Figure 3.13a. Both crystal structures may be generated by the stacking of these close-packed planes on top of one another; the difference between the two structures lies in the stacking sequence.

Let the centers of all the atoms in one close-packed plane be labeled A. Associated with this plane are two sets of equivalent triangular depressions formed by three adjacent atoms, into which the next close-packed plane of atoms may rest. Those having the triangle vertex pointing up are arbitrarily designated as B positions, while the remaining depressions are those with the down vertices, which are marked C in Figure 3.13a.

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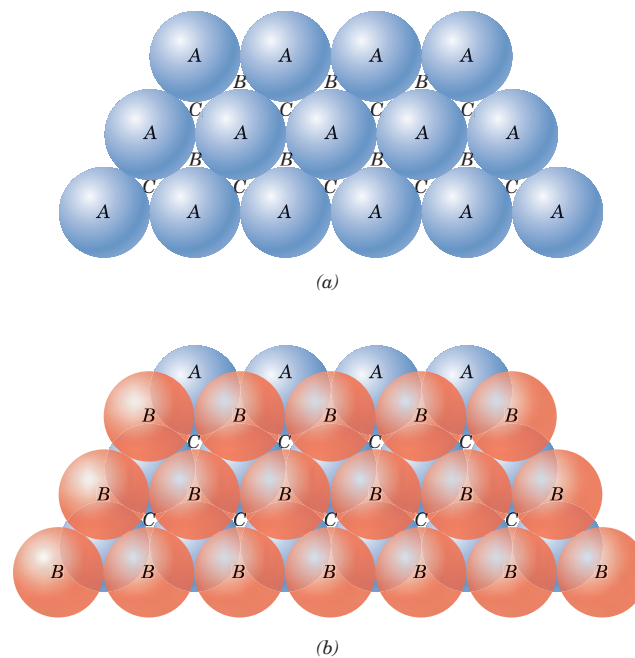


Figure 3.13 (a) A portion of a close-packed plane of atoms; A , B , and C positions are indicated. (b) The AB stacking sequence for close-packed atomic planes. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 50. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

A second close-packed plane may be positioned with the centers of its atoms over either B or C sites; at this point both are equivalent. Suppose that the B positions are arbitrarily chosen; the stacking sequence is termed AB , which is illustrated in Figure 3.13b. The real distinction between FCC and HCP lies in where the third close-packed layer is positioned. For HCP, the centers of this layer are aligned directly above the original A positions. This stacking sequence, $ABABAB \dots$, is repeated over and over. Of course, the $ACACAC \dots$ arrangement would be equivalent. These close-packed planes for HCP are (0001)-type planes, and the correspondence between this and the unit cell representation is shown in Figure 3.14.

For the face-centered crystal structure, the centers of the third plane are situated over the C sites of the first plane (Figure 3.15a). This yields an $ABCABCABC \dots$

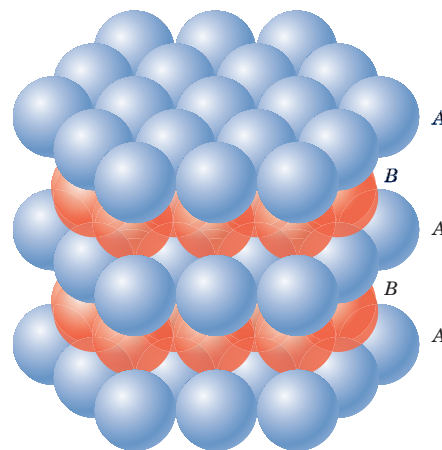


Figure 3.14 Close-packed plane stacking sequence for hexagonal close-packed. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

3.13 Single Crystals • 63

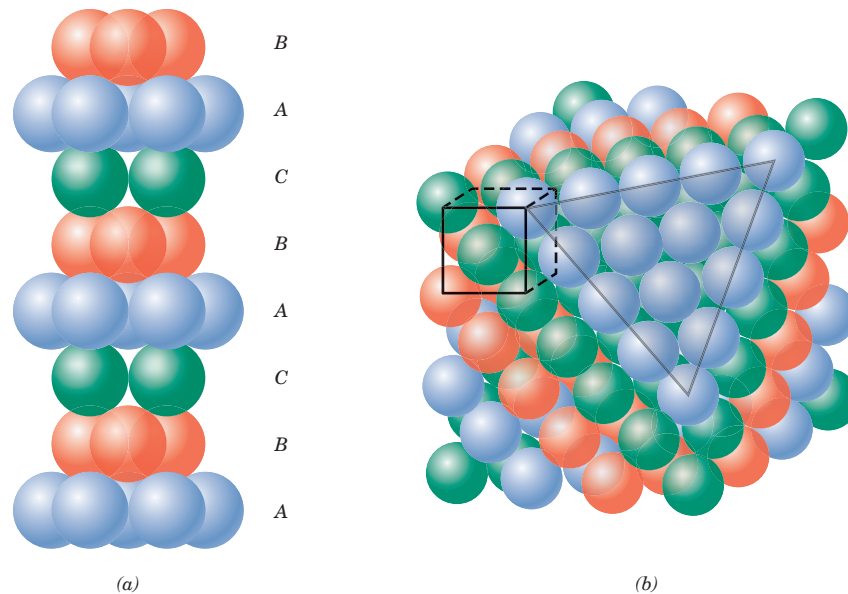


Figure 3.15 (a) Close-packed stacking sequence for face-centered cubic. (b) A corner has been removed to show the relation between the stacking of close-packed planes of atoms and the FCC crystal structure; the heavy triangle outlines a (111) plane. [Figure (b) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.]

stacking sequence; that is, the atomic alignment repeats every third plane. It is more difficult to correlate the stacking of close-packed planes to the FCC unit cell. However, this relationship is demonstrated in Figure 3.15b. These planes are of the (111) type; an FCC unit cell is outlined on the upper left-hand front face of Figure 3.15b, in order to provide a perspective. The significance of these FCC and HCP close-packed planes will become apparent in Chapter 7.

The concepts detailed in the previous four sections also relate to crystalline ceramic and polymeric materials, which are discussed in Chapters 12 and 14. We may specify crystallographic planes and directions in terms of directional and Miller indices; furthermore, on occasion it is important to ascertain the atomic and ionic arrangements of particular crystallographic planes. Also, the crystal structures of a number of ceramic materials may be generated by the stacking of close-packed planes of ions (Section 12.2).

Crystalline and Noncrystalline Materials

3.13 SINGLE CRYSTALS

single crystal

For a crystalline solid, when the periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption, the result is a **single crystal**. All unit cells interlock in the same way and have the same

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Figure 3.16
Photograph of a garnet single crystal that was found in Tongbei, Fujian Province, China. (Photograph courtesy of Irocks.com, Megan Foreman photo.)

orientation. Single crystals exist in nature, but they may also be produced artificially. They are ordinarily difficult to grow, because the environment must be carefully controlled.

If the extremities of a single crystal are permitted to grow without any external constraint, the crystal will assume a regular geometric shape having flat faces, as with some of the gem stones; the shape is indicative of the crystal structure. A photograph of a garnet single crystal is shown in Figure 3.16. Within the past few years, single crystals have become extremely important in many of our modern technologies, in particular electronic microcircuits, which employ single crystals of silicon and other semiconductors.

3.14 POLYCRYSTALLINE MATERIALS

grain

polycrystalline

grain boundary

Most crystalline solids are composed of a collection of many small crystals or **grains**; such materials are termed **polycrystalline**. Various stages in the solidification of a polycrystalline specimen are represented schematically in Figure 3.17. Initially, small crystals or nuclei form at various positions. These have random crystallographic orientations, as indicated by the square grids. The small grains grow by the successive addition from the surrounding liquid of atoms to the structure of each. The extremities of adjacent grains impinge on one another as the solidification process approaches completion. As indicated in Figure 3.17, the crystallographic orientation varies from grain to grain. Also, there exists some atomic mismatch within the region where two grains meet; this area, called a **grain boundary**, is discussed in more detail in Section 4.6.

3.15 ANISOTROPY

anisotropy

isotropic

The physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken. For example, the elastic modulus, the electrical conductivity, and the index of refraction may have different values in the [100] and [111] directions. This directionality of properties is termed **anisotropy**, and it is associated with the variance of atomic or ionic spacing with crystallographic direction. Substances in which measured properties are independent of the direction of measurement are **isotropic**. The extent and magnitude of

3.15 Anisotropy • 65

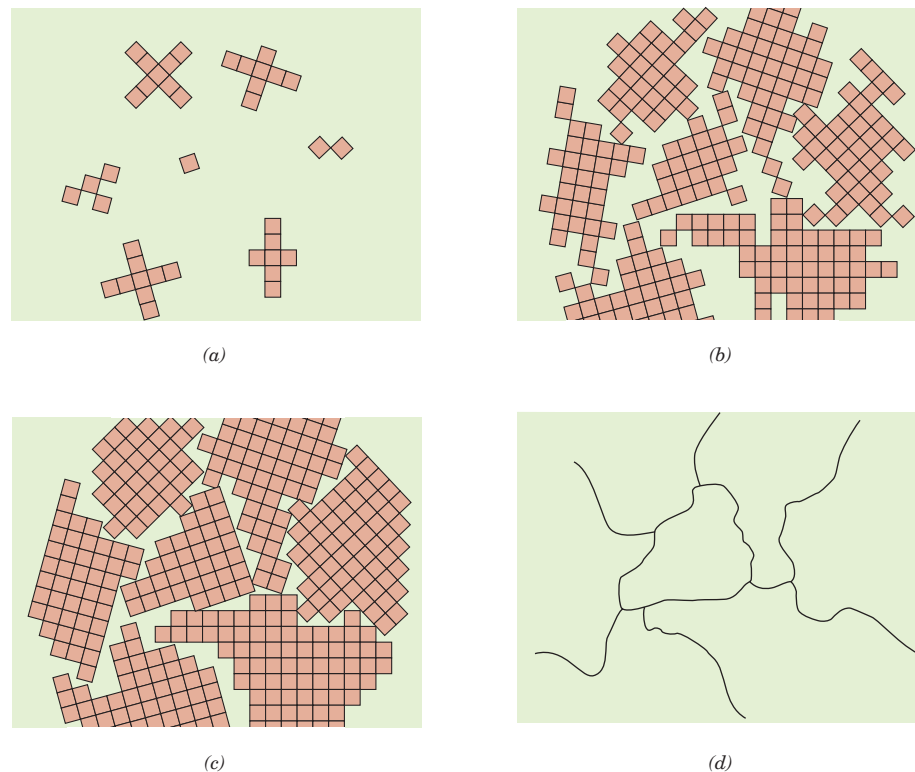


Figure 3.17 Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (a) Small crystallite nuclei. (b) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (c) Upon completion of solidification, grains having irregular shapes have formed. (d) The grain structure as it would appear under the microscope; dark lines are the grain boundaries. (Adapted from W. Rosenhain, *An Introduction to the Study of Physical Metallurgy*, 2nd edition, Constable & Company Ltd., London, 1915.)

anisotropic effects in crystalline materials are functions of the symmetry of the crystal structure; the degree of anisotropy increases with decreasing structural symmetry—triclinic structures normally are highly anisotropic. The modulus of elasticity values at $[100]$, $[110]$, and $[111]$ orientations for several materials are presented in Table 3.3.

For many polycrystalline materials, the crystallographic orientations of the individual grains are totally random. Under these circumstances, even though each grain may be anisotropic, a specimen composed of the grain aggregate behaves isotropically. Also, the magnitude of a measured property represents some average of the directional values. Sometimes the grains in polycrystalline materials have a preferential crystallographic orientation, in which case the material is said to have a “texture.”

The magnetic properties of some iron alloys used in transformer cores are anisotropic—that is, grains (or single crystals) magnetize in a $\langle 100 \rangle$ -type direction easier than any other crystallographic direction. Energy losses in transformer cores are minimized by utilizing polycrystalline sheets of these alloys into which have been introduced a “magnetic texture”: most of the grains in each sheet have a

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Table 3.3 Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

Metal	Modulus of Elasticity (GPa)		
	[100]	[110]	[111]
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

$\langle 100 \rangle$ -type crystallographic direction that is aligned (or almost aligned) in the same direction, which direction is oriented parallel to the direction of the applied magnetic field. Magnetic textures for iron alloys are discussed in detail in the Materials of Importance piece in Chapter 20 following Section 20.9.

3.16 X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Historically, much of our understanding regarding the atomic and molecular arrangements in solids has resulted from x-ray diffraction investigations; furthermore, x-rays are still very important in developing new materials. We will now give a brief overview of the diffraction phenomenon and how, using x-rays, atomic interplanar distances and crystal structures are deduced.

The Diffraction Phenomenon

Diffraction occurs when a wave encounters a series of regularly spaced obstacles that (1) are capable of scattering the wave, and (2) have spacings that are comparable in magnitude to the wavelength. Furthermore, diffraction is a consequence of specific phase relationships established between two or more waves that have been scattered by the obstacles.

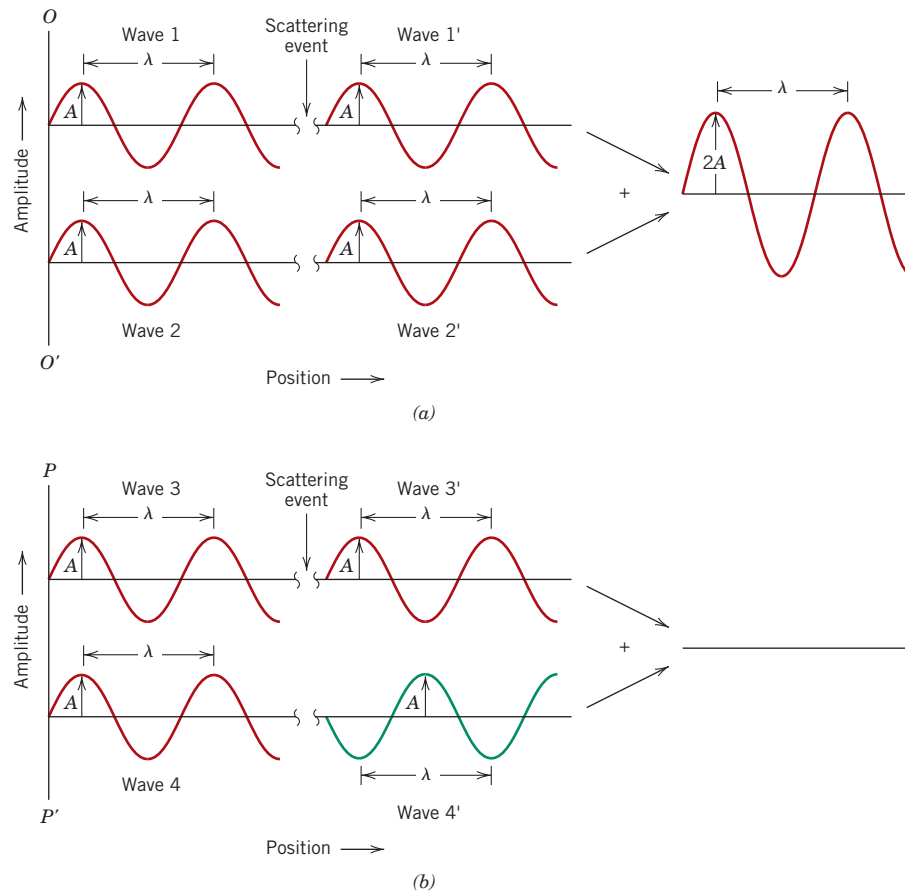
Consider waves 1 and 2 in Figure 3.18a which have the same wavelength (λ) and are in phase at point $O-O'$. Now let us suppose that both waves are scattered in such a way that they traverse different paths. The phase relationship between the scattered waves, which will depend upon the difference in path length, is important. One possibility results when this path length difference is an integral number of wavelengths. As noted in Figure 3.18a, these scattered waves (now labeled 1' and 2') are still in phase. They are said to mutually reinforce (or constructively interfere with) one another; and, when amplitudes are added, the wave shown on the right side of the figure results. This is a manifestation of **diffraction**, and we refer to a diffracted beam as one composed of a large number of scattered waves that mutually reinforce one another.

Other phase relationships are possible between scattered waves that will not lead to this mutual reinforcement. The other extreme is that demonstrated in Figure 3.18b, wherein the path length difference after scattering is some integral number of *half* wavelengths. The scattered waves are out of phase—that is, corresponding amplitudes cancel or annul one another, or destructively interfere (i.e., the

diffraction

3.16 X-Ray Diffraction: Determination of Crystal Structures • 67

Figure 3.18
 (a) Demonstration of how two waves (labeled 1 and 2) that have the same wavelength λ and remain in phase after a scattering event (waves 1' and 2') constructively interfere with one another. The amplitudes of the scattered waves add together in the resultant wave.
 (b) Demonstration of how two waves (labeled 3 and 4) that have the same wavelength and become out of phase after a scattering event (waves 3' and 4') destructively interfere with one another. The amplitudes of the two scattered waves cancel one another.



resultant wave has zero amplitude), as indicated on the extreme right side of the figure. Of course, phase relationships intermediate between these two extremes exist, resulting in only partial reinforcement.

X-Ray Diffraction and Bragg's Law

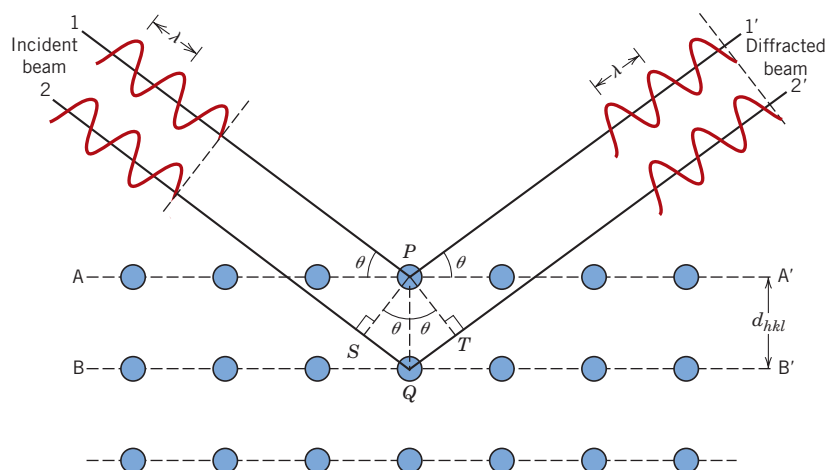
X-rays are a form of electromagnetic radiation that have high energies and short wavelengths—wavelengths on the order of the atomic spacings for solids. When a beam of x-rays impinges on a solid material, a portion of this beam will be scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path. Let us now examine the necessary conditions for diffraction of x-rays by a periodic arrangement of atoms.

Consider the two parallel planes of atoms A–A' and B–B' in Figure 3.19, which have the same h , k , and l Miller indices and are separated by the interplanar spacing d_{hkl} . Now assume that a parallel, monochromatic, and coherent (in-phase) beam of x-rays of wavelength λ is incident on these two planes at an angle θ . Two rays in this beam, labeled 1 and 2, are scattered by atoms P and Q . Constructive interference of the scattered rays 1' and 2' occurs also at an angle θ to the planes, if the path length difference between 1–P–1' and 2–Q–2' (i.e., $\overline{SQ} + \overline{QT}$) is equal to a whole number, n , of wavelengths. That is, the condition for diffraction is

$$n\lambda = \overline{SQ} + \overline{QT} \quad (3.12)$$

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Figure 3.19
Diffraction of x-rays
by planes of atoms
(A–A' and B–B').



Bragg's law—
relationship among
x-ray wavelength,
interatomic spacing,
and angle of
diffraction for
constructive
interference

Bragg's law

Interplanar
separation for a
plane having indices
 h , k , and l

or

$$\begin{aligned} n\lambda &= d_{hkl} \sin \theta + d_{hkl} \sin \theta \\ &= 2d_{hkl} \sin \theta \end{aligned} \quad (3.13)$$

Equation 3.13 is known as **Bragg's law**; also, n is the order of reflection, which may be any integer (1, 2, 3, ...) consistent with $\sin \theta$ not exceeding unity. Thus, we have a simple expression relating the x-ray wavelength and interatomic spacing to the angle of the diffracted beam. If Bragg's law is not satisfied, then the interference will be nonconstructive in nature so as to yield a very low-intensity diffracted beam.

The magnitude of the distance between two adjacent and parallel planes of atoms (i.e., the interplanar spacing d_{hkl}) is a function of the Miller indices (h , k , and l) as well as the lattice parameter(s). For example, for crystal structures that have cubic symmetry,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3.14)$$

in which a is the lattice parameter (unit cell edge length). Relationships similar to Equation 3.14, but more complex, exist for the other six crystal systems noted in Table 3.2.

Bragg's law, Equation 3.13, is a necessary but not sufficient condition for diffraction by real crystals. It specifies when diffraction will occur for unit cells having atoms positioned only at cell corners. However, atoms situated at other sites (e.g., face and interior unit cell positions as with FCC and BCC) act as extra scattering centers, which can produce out-of-phase scattering at certain Bragg angles. The net result is the absence of some diffracted beams that, according to Equation 3.13, should be present. For example, for the BCC crystal structure, $h + k + l$ must be even if diffraction is to occur, whereas for FCC, h , k , and l must all be either odd or even.

3.16 X-Ray Diffraction: Determination of Crystal Structures • 69

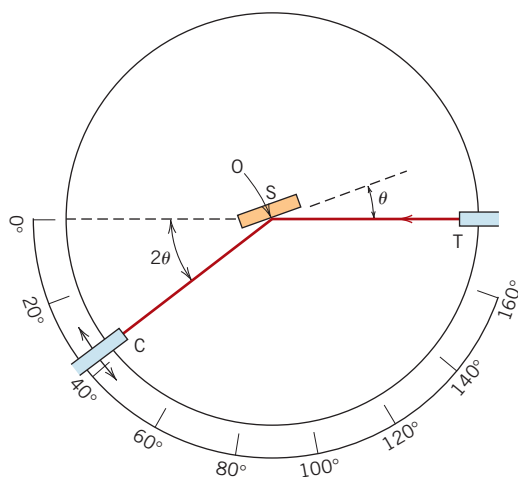


Figure 3.20 Schematic diagram of an x-ray diffractometer; T = x-ray source, S = specimen, C = detector, and O = the axis around which the specimen and detector rotate.



Concept Check 3.2

For cubic crystals, as values of the planar indices h , k , and l increase, does the distance between adjacent and parallel planes (i.e., the interplanar spacing) increase or decrease? Why?

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

Diffraction Techniques

One common diffraction technique employs a powdered or polycrystalline specimen consisting of many fine and randomly oriented particles that are exposed to monochromatic x-radiation. Each powder particle (or grain) is a crystal, and having a large number of them with random orientations ensures that some particles are properly oriented such that every possible set of crystallographic planes will be available for diffraction.

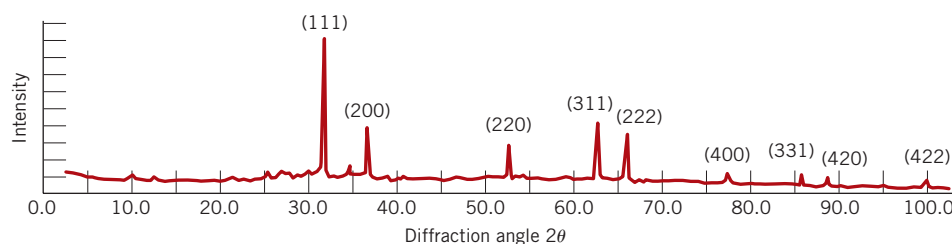
The *diffractometer* is an apparatus used to determine the angles at which diffraction occurs for powdered specimens; its features are represented schematically in Figure 3.20. A specimen S in the form of a flat plate is supported so that rotations about the axis labeled O are possible; this axis is perpendicular to the plane of the page. The monochromatic x-ray beam is generated at point T, and the intensities of diffracted beams are detected with a counter labeled C in the figure. The specimen, x-ray source, and counter are all coplanar.

The counter is mounted on a movable carriage that may also be rotated about the O axis; its angular position in terms of 2θ is marked on a graduated scale.⁴ Carriage and specimen are mechanically coupled such that a rotation of the specimen through θ is accompanied by a 2θ rotation of the counter; this assures that the incident and reflection angles are maintained equal to one another (Figure 3.20).

⁴ Note that the symbol θ has been used in two different contexts for this discussion. Here, θ represents the angular locations of both x-ray source and counter relative to the specimen surface. Previously (e.g., Equation 3.13), it denoted the angle at which the Bragg criterion for diffraction is satisfied.

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Figure 3.21
Diffraction pattern
for powdered lead.
(Courtesy of Wesley
L. Holman.)



Collimators are incorporated within the beam path to produce a well-defined and focused beam. Utilization of a filter provides a near-monochromatic beam.

As the counter moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity (monitored by the counter) as a function of 2θ ; 2θ is termed the *diffraction angle*, which is measured experimentally. Figure 3.21 shows a diffraction pattern for a powdered specimen of lead. The high-intensity peaks result when the Bragg diffraction condition is satisfied by some set of crystallographic planes. These peaks are plane-indexed in the figure.

Other powder techniques have been devised wherein diffracted beam intensity and position are recorded on a photographic film instead of being measured by a counter.

One of the primary uses of x-ray diffractometry is for the determination of crystal structure. The unit cell size and geometry may be resolved from the angular positions of the diffraction peaks, whereas arrangement of atoms within the unit cell is associated with the relative intensities of these peaks.

X-rays, as well as electron and neutron beams, are also used in other types of material investigations. For example, crystallographic orientations of single crystals are possible using x-ray diffraction (or Laue) photographs. In the (a) chapter-opening photograph for this chapter is shown a photograph that was generated using an incident x-ray beam that was directed on a magnesium crystal; each spot (with the exception of the darkest one near the center) resulted from an x-ray beam that was diffracted by a specific set of crystallographic planes. Other uses of x-rays include qualitative and quantitative chemical identifications and the determination of residual stresses and crystal size.

EXAMPLE PROBLEM 3.12

Interplanar Spacing and Diffraction Angle Computations

For BCC iron, compute (a) the interplanar spacing, and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Also, assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

Solution

(a) The value of the interplanar spacing d_{hkl} is determined using Equation 3.14, with $a = 0.2866$ nm, and $h = 2$, $k = 2$, and $l = 0$, since we are considering the (220) planes. Therefore,

$$\begin{aligned} d_{hkl} &= \frac{a}{\sqrt{h^2 + k^2 + l^2}} \\ &= \frac{0.2866 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.1013 \text{ nm} \end{aligned}$$

3.17 Noncrystalline Solids • 71

(b) The value of θ may now be computed using Equation 3.13, with $n = 1$, since this is a first-order reflection:

$$\sin \theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790 \text{ nm})}{(2)(0.1013 \text{ nm})} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13^\circ$$

The diffraction angle is 2θ , or

$$2\theta = (2)(62.13^\circ) = 124.26^\circ$$

3.17 NONCRYSTALLINE SOLIDS

noncrystalline

amorphous

It has been mentioned that **noncrystalline** solids lack a systematic and regular arrangement of atoms over relatively large atomic distances. Sometimes such materials are also called **amorphous** (meaning literally without form), or supercooled liquids, inasmuch as their atomic structure resembles that of a liquid.

An amorphous condition may be illustrated by comparison of the crystalline and noncrystalline structures of the ceramic compound silicon dioxide (SiO_2), which may exist in both states. Figures 3.22a and 3.22b present two-dimensional schematic diagrams for both structures of SiO_2 . Even though each silicon ion bonds to three oxygen ions for both states, beyond this, the structure is much more disordered and irregular for the noncrystalline structure.

Whether a crystalline or amorphous solid forms depends on the ease with which a random atomic structure in the liquid can transform to an ordered state during solidification. Amorphous materials, therefore, are characterized by atomic or molecular structures that are relatively complex and become ordered only with some difficulty. Furthermore, rapidly cooling through the freezing temperature favors the formation of a noncrystalline solid, since little time is allowed for the ordering process.

Metals normally form crystalline solids, but some ceramic materials are crystalline, whereas others, the inorganic glasses, are amorphous. Polymers may be completely

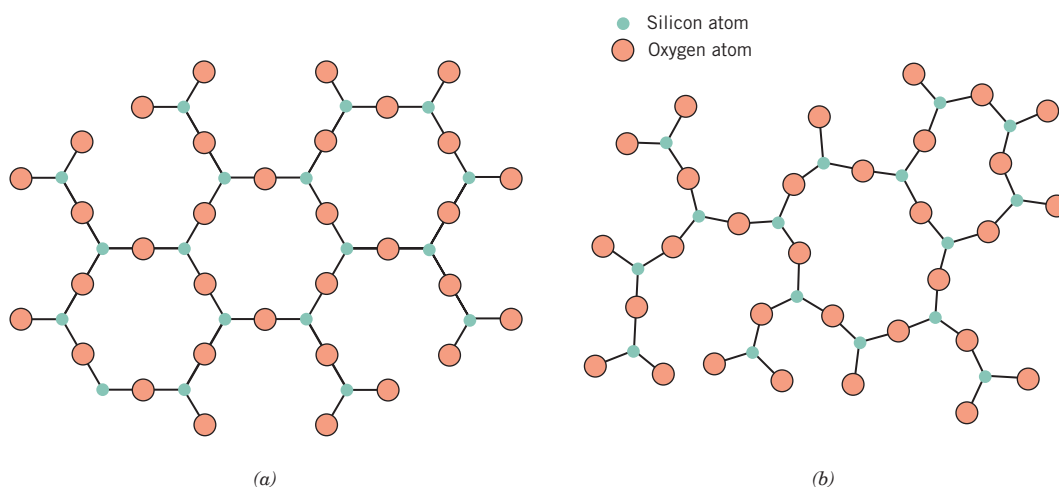


Figure 3.22 Two-dimensional schemes of the structure of (a) crystalline silicon dioxide and (b) noncrystalline silicon dioxide.

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noncrystalline and semicrystalline consisting of varying degrees of crystallinity. More about the structure and properties of amorphous ceramics and polymers is contained in Chapters 12 and 14.

**Concept Check 3.3**

Do noncrystalline materials display the phenomenon of allotropy (or polymorphism)? Why or why not?

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

SUMMARY**Fundamental Concepts****Unit Cells**

Atoms in crystalline solids are positioned in orderly and repeated patterns that are in contrast to the random and disordered atomic distribution found in noncrystalline or amorphous materials. Atoms may be represented as solid spheres, and, for crystalline solids, crystal structure is just the spatial arrangement of these spheres. The various crystal structures are specified in terms of parallelepiped unit cells, which are characterized by geometry and atom positions within.

Metallic Crystal Structures

Most common metals exist in at least one of three relatively simple crystal structures: face-centered cubic (FCC), body-centered cubic (BCC), and hexagonal close-packed (HCP). Two features of a crystal structure are coordination number (or number of nearest-neighbor atoms) and atomic packing factor (the fraction of solid sphere volume in the unit cell). Coordination number and atomic packing factor are the same for both FCC and HCP crystal structures, each of which may be generated by the stacking of close-packed planes of atoms.

Point Coordinates**Crystallographic Directions****Crystallographic Planes**

Crystallographic points, directions, and planes are specified in terms of indexing schemes. The basis for the determination of each index is a coordinate axis system defined by the unit cell for the particular crystal structure. The location of a point within a unit cell is specified using coordinates that are fractional multiples of the cell edge lengths. Directional indices are computed in terms of the vector projection on each of the coordinate axes, whereas planar indices are determined from the reciprocals of axial intercepts. For hexagonal unit cells, a four-index scheme for both directions and planes is found to be more convenient.

Linear and Planar Densities

Crystallographic directional and planar equivalencies are related to atomic linear and planar densities, respectively. The atomic packing (i.e., planar density) of spheres

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in a crystallographic plane depends on the indices of the plane as well as the crystal structure. For a given crystal structure, planes having identical atomic packing yet different Miller indices belong to the same family.

Single Crystals Polycrystalline Materials

Single crystals are materials in which the atomic order extends uninterrupted over the entirety of the specimen; under some circumstances, they may have flat faces and regular geometric shapes. The vast majority of crystalline solids, however, are polycrystalline, being composed of many small crystals or grains having different crystallographic orientations.

Crystal Systems Polymorphism and Allotropy Anisotropy

Other concepts introduced in this chapter were: crystal system (a classification scheme for crystal structures on the basis of unit cell geometry), polymorphism (or allotropy) (when a specific material can have more than one crystal structure), and anisotropy (the directionality dependence of properties).

X-Ray Diffraction: Determination of Crystal Structures

X-ray diffractometry is used for crystal structure and interplanar spacing determinations. A beam of x-rays directed on a crystalline material may experience diffraction (constructive interference) as a result of its interaction with a series of parallel atomic planes according to Bragg's law. Interplanar spacing is a function of the Miller indices and lattice parameter(s) as well as the crystal structure.

IMPORTANT TERMS AND CONCEPTS

Allotropy	Crystal system	Lattice
Amorphous	Crystalline	Lattice parameters
Anisotropy	Diffraction	Miller indices
Atomic packing factor (APF)	Face-centered cubic (FCC)	Noncrystalline
Body-centered cubic (BCC)	Grain	Polycrystalline
Bragg's law	Grain boundary	Polymorphism
Coordination number	Hexagonal close-packed (HCP)	Single crystal
Crystal structure	Isotropic	Unit cell

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|--|---|
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QUESTIONS AND PROBLEMS

Fundamental Concepts

- 3.1 What is the difference between atomic structure and crystal structure?

Unit Cells

Metallic Crystal Structures

- 3.2 If the atomic radius of lead is 0.175 nm, calculate the volume of its unit cell in cubic meters.
- 3.3 Show for the body-centered cubic crystal structure that the unit cell edge length a and the atomic radius R are related through $a = 4R/\sqrt{3}$.
- 3.4 For the HCP crystal structure, show that the ideal c/a ratio is 1.633.
- 3.5 Show that the atomic packing factor for BCC is 0.68.
- 3.6 Show that the atomic packing factor for HCP is 0.74.

Density Computations

- 3.7 Molybdenum has a BCC crystal structure, an atomic radius of 0.1363 nm, and an atomic weight of 95.94 g/mol. Compute and compare its theoretical density with the experimental value found inside the front cover.
- 3.8 Calculate the radius of a palladium atom, given that Pd has an FCC crystal structure, a density of 12.0 g/cm³, and an atomic weight of 106.4 g/mol.
- 3.9 Calculate the radius of a tantalum atom, given that Ta has a BCC crystal structure, a density of 16.6 g/cm³, and an atomic weight of 180.9 g/mol.
- 3.10 Some hypothetical metal has the simple cubic crystal structure shown in Figure 3.23. If its atomic weight is 74.5 g/mol and the atomic radius is 0.145 nm, compute its density.

- 3.11 Titanium has an HCP crystal structure and a density of 4.51 g/cm³.

- (a) What is the volume of its unit cell in cubic meters?
- (b) If the c/a ratio is 1.58, compute the values of c and a .

- 3.12 Using atomic weight, crystal structure, and atomic radius data tabulated inside the front cover, compute the theoretical densities of aluminum, nickel, magnesium, and tungsten, and then compare these values with the measured densities listed in this same table. The c/a ratio for magnesium is 1.624.

- 3.13 Niobium has an atomic radius of 0.1430 nm and a density of 8.57 g/cm³. Determine whether it has an FCC or BCC crystal structure.

- 3.14 Below are listed the atomic weight, density, and atomic radius for three hypothetical alloys. For each determine whether its crystal structure is FCC, BCC, or simple cubic and then justify your determination. A simple cubic unit cell is shown in Figure 3.23.

Alloy	Atomic Weight (g/mol)	Density (g/cm ³)	Atomic Radius (nm)
A	43.1	6.40	0.122
B	184.4	12.30	0.146
C	91.6	9.60	0.137

- 3.15 The unit cell for uranium has orthorhombic symmetry, with a , b , and c lattice parameters of 0.286, 0.587, and 0.495 nm, respectively. If its density, atomic weight, and atomic radius are 19.05 g/cm³, 238.03 g/mol, and 0.1385 nm, respectively, compute the atomic packing factor.

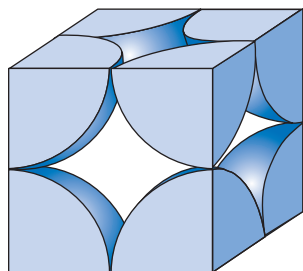


Figure 3.23 Hard-sphere unit cell representation of the simple cubic crystal structure.

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3.16 Indium has a tetragonal unit cell for which the a and c lattice parameters are 0.459 and 0.495 nm, respectively.

(a) If the atomic packing factor and atomic radius are 0.693 and 0.1625 nm, respectively, determine the number of atoms in each unit cell.

(b) The atomic weight of indium is 114.82 g/mol; compute its theoretical density.

3.17 Beryllium has an HCP unit cell for which the ratio of the lattice parameters c/a is 1.568. If the radius of the Be atom is 0.1143 nm, (a) determine the unit cell volume, and (b) calculate the theoretical density of Be and compare it with the literature value.

3.18 Magnesium has an HCP crystal structure, a c/a ratio of 1.624, and a density of 1.74 g/cm³. Compute the atomic radius for Mg.

3.19 Cobalt has an HCP crystal structure, an atomic radius of 0.1253 nm, and a c/a ratio of 1.623. Compute the volume of the unit cell for Co.

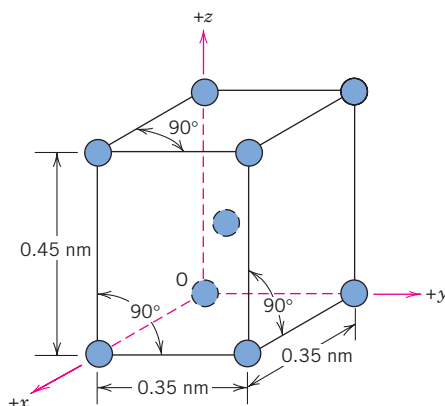
Crystal Systems

3.20 Below is a unit cell for a hypothetical metal.

(a) To which crystal system does this unit cell belong?

(b) What would this crystal structure be called?

(c) Calculate the density of the material, given that its atomic weight is 141 g/mol.



3.21 Sketch a unit cell for the face-centered orthorhombic crystal structure.

Point Coordinates

3.22 List the point coordinates for all atoms that are associated with the FCC unit cell (Figure 3.1).

3.23 List the point coordinates of both the sodium and chlorine ions for a unit cell of the sodium chloride crystal structure (Figure 12.2).

3.24 List the point coordinates of both the zinc and sulfur atoms for a unit cell of the zinc blende crystal structure (Figure 12.4).

3.25 Sketch a tetragonal unit cell, and within that cell indicate locations of the $1\ 1\ \frac{1}{2}$ and $\frac{1}{2}\ \frac{1}{4}\ \frac{1}{2}$ point coordinates.

3.26 Using the Molecule Definition Utility found in both “Metallic Crystal Structures and Crystallography” and “Ceramic Crystal Structures” modules of *VMSE*, located on the book’s web site [www.wiley.com/college/callister (Student Companion Site)], generate (and print out) a three-dimensional unit cell for β tin given the following: (1) the unit cell is tetragonal with $a = 0.583$ nm and $c = 0.318$ nm, and (2) Sn atoms are located at the following point coordinates:

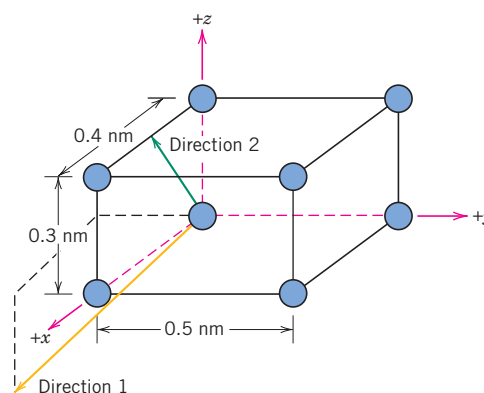
0 0 0	0 1 1
1 0 0	$\frac{1}{2}\ 0\ \frac{3}{4}$
1 1 0	$\frac{1}{2}\ 1\ \frac{3}{4}$
0 1 0	$1\ \frac{1}{2}\ \frac{1}{4}$
0 0 1	$0\ \frac{1}{2}\ \frac{1}{4}$
1 0 1	$\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$
1 1 1	

Crystallographic Directions

3.27 Draw an orthorhombic unit cell, and within that cell a $[2\bar{1}1]$ direction.

3.28 Sketch a monoclinic unit cell, and within that cell a $[\bar{1}01]$ direction.

3.29 What are the indices for the directions indicated by the two vectors in the sketch below?



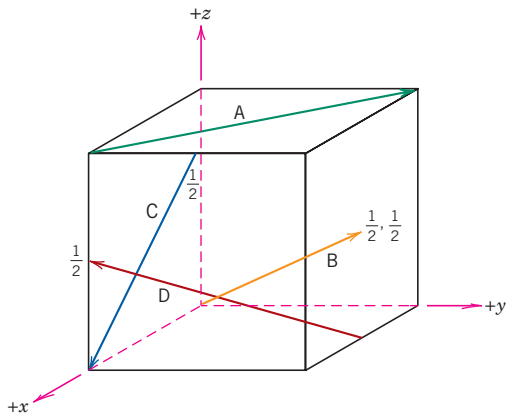
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3.30 Within a cubic unit cell, sketch the following directions:

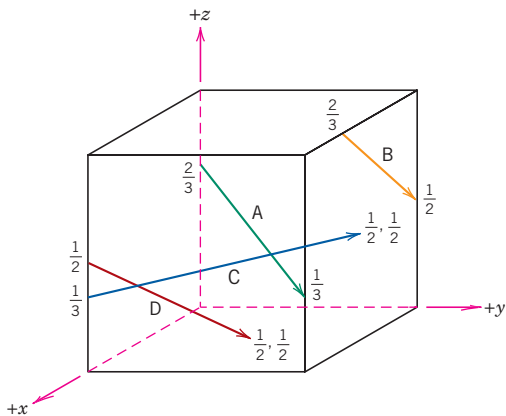


- (a) $[101]$, (e) $[\bar{1}\bar{1}\bar{1}]$,
 (b) $[211]$, (f) $[\bar{2}12]$,
 (c) $[10\bar{2}]$, (g) $[3\bar{1}2]$,
 (d) $[3\bar{1}3]$, (h) $[301]$.

3.31 Determine the indices for the directions shown in the following cubic unit cell:



3.32 Determine the indices for the directions shown in the following cubic unit cell:

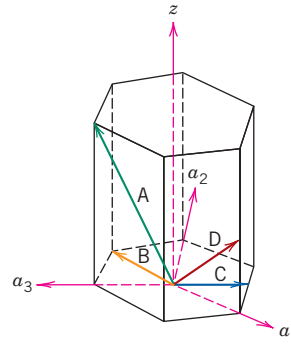


3.33 For tetragonal crystals, cite the indices of directions that are equivalent to each of the following directions:

- (a) $[011]$
 (b) $[100]$

3.34 Convert the $[110]$ and $[00\bar{1}]$ directions into the four-index Miller–Bravais scheme for hexagonal unit cells.

3.35 Determine the indices for the directions shown in the following hexagonal unit cell:



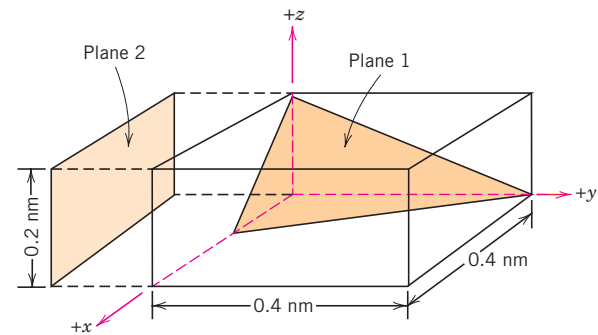
3.36 Using Equations 3.6a, 3.6b, 3.6c, and 3.6d, derive expressions for each of the three primed indices set (u' , v' , and w') in terms of the four unprimed indices (u , v , t , and w).

Crystallographic Planes

3.37 (a) Draw an orthorhombic unit cell, and within that cell a $(02\bar{1})$ plane.

(b) Draw a monoclinic unit cell, and within that cell a (200) plane.

3.38 What are the indices for the two planes drawn in the sketch below?



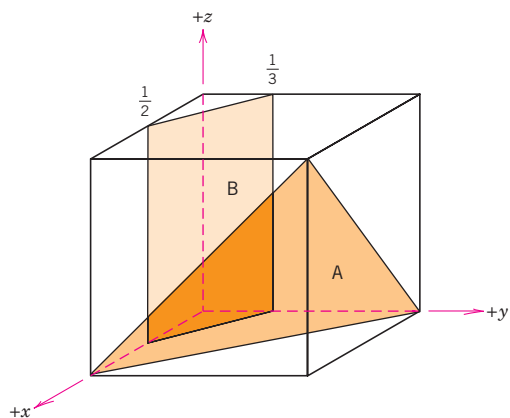
3.39 Sketch within a cubic unit cell the following planes:



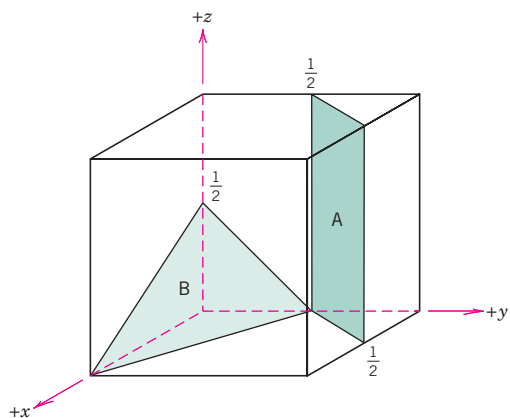
- (a) $(10\bar{1})$, (e) $(\bar{1}\bar{1}\bar{1})$,
 (b) $(2\bar{1}1)$, (f) $(\bar{2}12)$,
 (c) (012) , (g) $(3\bar{1}2)$,
 (d) $(3\bar{1}3)$, (h) (301) .

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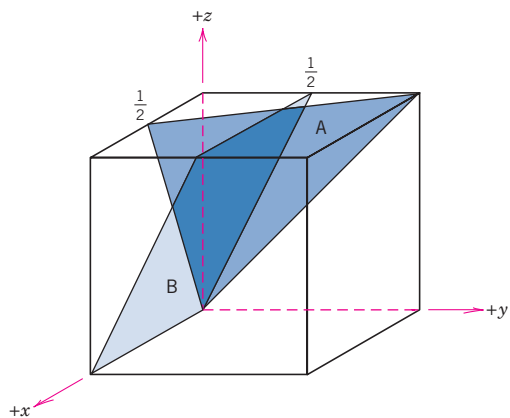
- 3.40** Determine the Miller indices for the planes shown in the following unit cell:



- 3.41** Determine the Miller indices for the planes shown in the following unit cell:



- 3.42** Determine the Miller indices for the planes shown in the following unit cell:



- 3.43** Cite the indices of the direction that results from the intersection of each of the following pair of planes within a cubic crystal: **(a)** (110)

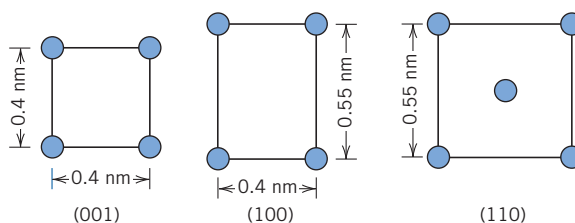
and (111) planes, **(b)** (110) and $(\bar{1}\bar{1}0)$ planes, and **(c)** $(11\bar{1})$ and (001) planes.

- 3.44** Sketch the atomic packing of **(a)** the (100) plane for the FCC crystal structure, and **(b)** the (111) plane for the BCC crystal structure (similar to Figures 3.10b and 3.11b).

- 3.45** Consider the reduced-sphere unit cell shown in Problem 3.20, having an origin of the coordinate system positioned at the atom labeled with an O. For the following sets of planes, determine which are equivalent:

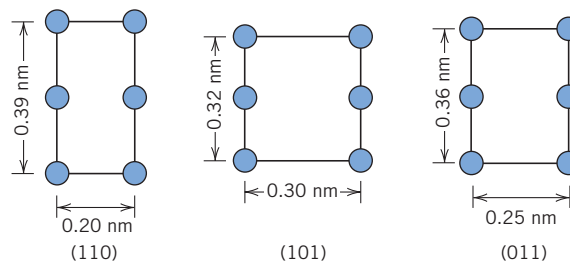
- (a)** (100), $(0\bar{1}0)$, and (001)
(b) (110), (101), (011), and $(\bar{1}01)$
(c) (111), $(1\bar{1}\bar{1})$, $(11\bar{1})$, and $(\bar{1}\bar{1}\bar{1})$

- 3.46** Here are three different crystallographic planes for a unit cell of a hypothetical metal. The circles represent atoms:



- (a)** To what crystal system does the unit cell belong?
(b) What would this crystal structure be called?

- 3.47** Below are shown three different crystallographic planes for a unit cell of some hypothetical metal. The circles represent atoms:

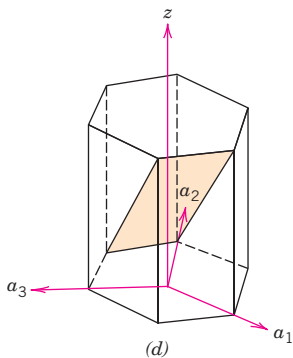
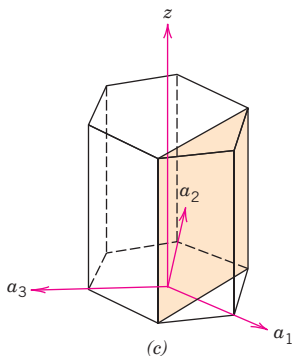
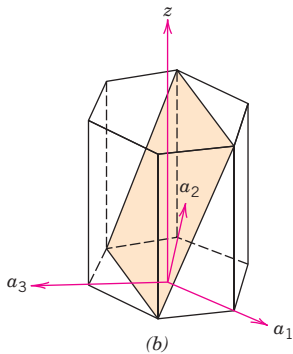
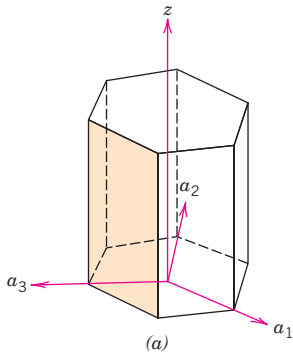


- (a)** To what crystal system does the unit cell belong?
(b) What would this crystal structure be called?
(c) If the density of this metal is 18.91 g/cm^3 , determine its atomic weight.

- 3.48** Convert the (111) and $(0\bar{1}2)$ planes into the four-index Miller–Bravais scheme for hexagonal unit cells.

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3.49 Determine the indices for the planes shown in the hexagonal unit cells below:



3.50 Sketch the $(01\bar{1}1)$ and $(2\bar{1}10)$ planes in a hexagonal unit cell.

Linear and Planar Densities

3.51 (a) Derive linear density expressions for FCC $[100]$ and $[111]$ directions in terms of the atomic radius R .

(b) Compute and compare linear density values for these same two planes for copper.

3.52 (a) Derive linear density expressions for BCC $[110]$ and $[111]$ directions in terms of the atomic radius R .

(b) Compute and compare linear density values for these same two planes for iron.

3.53 (a) Derive planar density expressions for FCC (100) and (111) planes in terms of the atomic radius R .

(b) Compute and compare planar density values for these same two planes for aluminum.

3.54 (a) Derive planar density expressions for BCC (100) and (110) planes in terms of the atomic radius R .

(b) Compute and compare planar density values for these same two planes for molybdenum.

3.55 (a) Derive the planar density expression for the HCP (0001) plane in terms of the atomic radius R .

(b) Compute the planar density value for this same plane for titanium.

Polycrystalline Materials

3.56 Explain why the properties of polycrystalline materials are most often isotropic.

X-Ray Diffraction: Determination of Crystal Structures

3.57 Using the data for aluminum in Table 3.1, compute the interplanar spacing for the (110) set of planes.

3.58 Determine the expected diffraction angle for the first-order reflection from the (310) set of planes for BCC chromium when monochromatic radiation of wavelength 0.0711 nm is used.

3.59 Using the data for α -iron in Table 3.1, compute the interplanar spacings for the (111) and (211) sets of planes.

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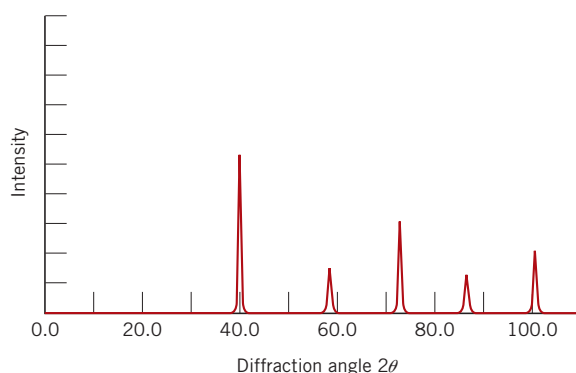


Figure 3.24 Diffraction pattern for powdered tungsten. (Courtesy of Wesley L. Holman.)

- 3.60** The metal rhodium has an FCC crystal structure. If the angle of diffraction for the (311) set of planes occurs at 36.12° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.0711 nm is used, compute (a) the interplanar spacing for this set of planes, and (b) the atomic radius for a rhodium atom.
- 3.61** The metal niobium has a BCC crystal structure. If the angle of diffraction for the (211) set of planes occurs at 75.99° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.1659 nm is used, compute (a) the interplanar spacing for this set of planes, and (b) the atomic radius for the niobium atom.
- 3.62** For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 44.53° for FCC nickel when monochromatic radiation having a wavelength of 0.1542 nm is used?
- 3.63** Figure 3.21 shows an x-ray diffraction pattern for lead taken using a diffractometer and monochromatic x-radiation having a wavelength of 0.1542 nm ; each diffraction peak on the pattern has been indexed. Compute the interplanar spacing for each set of planes indexed; also determine the lattice parameter of Pb for each of the peaks.
- 3.64** The diffraction peaks shown in Figure 3.21 are indexed according to the reflection rules for FCC (i.e., h , k , and l must all be either odd or even). Cite the h , k , and l indices of the first four diffraction peaks for BCC crystals consistent with $h + k + l$ being even.
- 3.65** Figure 3.24 shows the first five peaks of the x-ray diffraction pattern for tungsten, which has a BCC crystal structure; monochromatic x-radiation having a wavelength of 0.1542 nm was used.
- (a) Index (i.e., give h , k , and l indices) for each of these peaks.
- (b) Determine the interplanar spacing for each of the peaks.
- (c) For each peak, determine the atomic radius for W and compare these with the value presented in Table 3.1.

Noncrystalline Solids

- 3.66** Would you expect a material in which the atomic bonding is predominantly ionic in nature to be more or less likely to form a noncrystalline solid upon solidification than a covalent material? Why? (See Section 2.6.)